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EXCIMER POTENTIAL CURVES

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Summary

↘ The purpose of this project is the development of semi-empirical and theoretical methods of obtaining reasonably accurate potential curves for diatomic excimer systems. These curves are of importance for applications to fluorescence spectra, stimulated emission coefficients, excimer laser development and electron impact excitations. We have been mainly interested in the development of a new effective potential method which obtains potential curves by calculating the energy levels of one atom in the external field of the other atom. In order to be able to compare our new method to other well established methods, we have first done a CI calculation for GaKr and applied the Gordon-Kim method to GaKr. This provided some knowledge of the effect of a Kr atom on another atom which might be used later as input into the effective potential method.

The basic idea of the new method is as follows: In all low lying states of a metal-rare gas system one atom (the rare gas atom which has a high first excitation energy) is asymptotically in its ground state and the various molecular states correspond to the various low lying excited states of the metal atom. Therefore the basic assumption of our method is, that it is possible to calculate the molecular energy levels as the energy levels of a single metal atom in an external field which represents the rare gas atom. This external field which represents the second atom is our effective potential. The general form of this potential can be derived from the many body Greens function. Phenomenological treatments of the many body theory leads to a form with free parameters. Our idea is to determine these parameters by fitting one molecular potential curve, calculated by our new method, to a known curve. We hope that

the effective potential resulting from one particular state describes the effect of the rare gas atom also in other molecular states and even in other molecules, i.e. independently of the type and state of the other atom. The big problem in this new method is, that new types of integrals have occurred, which have not appeared in quantum chemistry before and for which no standard computer programs exist. Therefore, we spent most of the time developing and testing new computer programs. By now the programs seem to work properly but they are still very slow and at the moment we are still testing the whole method on a simple system, on LiHe. We have tried to parametrize the effective potential of the He ground state by fitting the resulting molecular potential for the 2π state of HeLi to the known potential curve of this state. Probably we did not use the best fitting strategy so far and therefore we did not get a satisfactory fit of the molecular potential. It seems to be necessary to repeat the fitting procedure with a more efficient strategy, which we consider in the text. The next step in the program, after the fit of the molecular potential curve for one state, is to calculate the molecular potential curves for other states of HeLi using the same effective potential to represent the He atom. The result of this test will show if the whole idea works or not. We are continuing work on this idea even without the support of ARPA-ONR as we believe it to be a valuable new method.

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§1

1.1 Introduction

The general purpose of this project is to continue the development and implementation of semi-empirical and theoretical methods of obtaining reasonably accurate potential curves for diatomic excimer systems.¹ Once the potential curves have been obtained, they can be used to predict fluorescence spectra², and to compute laser gain, stimulated emission coefficients³ and total cross sections for excitation by electron impact.⁴ While highly accurate potential curves are always a goal, our immediate goal is the relatively rapid production of potential curves that are accurate enough to guide experimentalists in choosing or rejecting possible laser systems on the basis of inexpensive theoretical calculations rather than on the basis of expensive and time-consuming experiments.

We are particularly interested in developing methods that in the future would be applicable to excimer systems because of the current emphasis on these systems as candidates for efficient, high-power visible and ultraviolet lasers.¹ The specific systems that motivated this proposal were the group IIA-, IIB- and IIIA-rare gas systems (such as MgXe and TlXe), alkali-group IIB systems and Thallium-group IIB systems. Our immediate goal is to develop a new efficient method to calculate potential curves for non-bonding diatomic systems in which the asymptotic atoms have greatly different ionization potentials (as do most metal-rare gas systems). We will then view the lowest several states of the molecule as roughly represented by a specific state of the metal in the effective "external" field of the high ionization potential (i.e. here a rare gas) atom.

The next step will be to parametrize this potential (and the effective electron potentials that arise therein) using a form suggested by field theory and data from any known molecular state of any metal-rare gas system that goes at large internuclear distance to the ground state of the rare gas. This effective potential will then be used to describe unknown states of the same or different metals by viewing their calculation as one of the metal atom in the field of this potential. If this aim is attained a basis empirical transfer of information from known to unknown systems and states will be achieved with an in principle accompanying simplification in calculations. This in turn would allow us to go to bigger systems.

Although extensive work has been done on calculating potential curves, the currently available methods are inadequate for large systems such as TlXe. While self-consistent field (SCF) and configuration interaction (CI) programs are the most accurate, at this time those computer codes cannot handle molecular systems with f electrons, such as TlXe.

Now, simplified methods, that are alternatives to CI do exist: The Gordon-Kim⁵ (GK) method is available but has not been adequately tested for large systems with open shells. We believe that our method, theoretically is better based than this method, as the reader can judge for himself in later sections, and it takes in such effects as mutual atomic polarization that the GK leaves out.

The most promising method for treating big systems rigorously is the pseudopotential method. The pseudopotential method⁶ is currently being extended to large systems.^{7,8}

The new method we are developing, the effective potential method, is essentially a means of calculating the potential curve for a diatomic system AB (where A is a closed shell atom) by doing an atomic SCF or CI calculation on B in which A is treated as an external (effective) potential. The effective potential is the sum of the Hartree-Fock potential for A and a polarization potential. The polarization potential consists of a one-particle part describing the polarization of A by an external charged particle and a two-particle part which corrects for the "depolarization" due to the presence of the other electrons and nucleus of B. The parameter of the effective potential will be obtained by using perturbation theory and a known potential curve of AX (X is any atom). If X is not highly polarized, a first order approximation to the effective potential U^A may be obtained by fitting the parameters to

$$V_{X,e}^A(R) = \int d\tau U^A(R,\tau) \rho_X(\tau)$$

where ρ_X is the density of atom X and $V_{X,e}^A$ is the electronic part of the known potential curve for AX. The theory of the effective potential and the perturbation treatment of it are discussed in more detail in §4.

This effective potential method has several advantages over the Gordon-Kim and pseudopotential methods. Because the effective potential allows for polarization of A and the SCF calculation allows for polarization of B, this method should be more accurate than GK. At the same time, LS coupling and relativistic effects can be included as easily in our method: the treatment of LS coupling would be the same and relativistic effects can be included in the core potentials. In comparing our effective potential method to pseudopotential methods, the following points should be noted. Methods which use only a pseudopotential to replace the valence-core inter-

actions do not include polarization of the core. In contrast, our method includes core polarization; consequently, the core-core interaction is correct at large distances so the correct van der Waals interaction will be obtained. Because we take advantage of the fact that there is no real bonding in the systems we are studying, our calculations will be essentially atomic calculations and will include fewer electrons explicitly than a pseudopotential calculation. Use of a semi-empirical potential which is parameterized to molecular data should result in better molecular potential curves than use of semi-empirical potentials parameterized to atomic data. In addition, use of molecular data will allow us to obtain effective potentials for electrons outside of rare gas atoms and for electrons outside of highly charged cores; these are two cases in which parameterization to atomic data would be extremely difficult.

Since the effective potential method is semi-empirical and since the potential parameters will be fit to molecular data, some potential curves are needed. Basically, there are two options available for parameterizing the effective potential of A in order to calculate potential curves for AB: 1) The effective potential for A can be fit to known potential curves for XA (where X is any atom) or 2) The effective potential for A can be fit to whatever ground and excited state curves for AB are known. The second option recognizes the facts that it is easier to obtain ground state curves than excited state curves by other methods and that both are needed to pick possible laser systems. The curves needed for fitting can be obtained by a variety of techniques varying from rigorous CI calculations to analysis of experimental data. As examples of available techniques, consider the following: When experimental band spectra data exist, the quasi-static theory of line shapes could be used to extract potentials.⁹ Atomic beam data (such as that supplied by Yuan Lee in Berkeley) could also be used to fit potential forms.¹⁰ The RKR method¹¹ could be used when, as is rarely the case in excimers, vibrational data exists. For positive-negative ion systems Rittner potentials¹² can be fit to available data. For systems with closed-shell separated atoms and ions or for certain types of open-shell

systems, the Gordon-Kim method⁵ can be used to predict short range potentials, and long range corrections can be added to this model. Short range repulsive potentials for closed-shell atoms and ions can also be fitted, correlated and interpolated using: (a) the delta-function model for homonuclear systems¹⁰; (b) the delta-function and distortion model with combination rules for heteronuclear systems¹⁰; (c) the related softness parameter methods that require atomic Hartree-Fock charge densities.¹³

Now after listing the advantages of our method we must admit to slow progress and a lack of success in so far completing our objectives due to two problems. The first is that our effective potential leads to new two center (atom-external potential) integrals such as those representing the interaction with the part of the effective potential representing the polarized rare gas (see later sections for details). We have developed methods and programs for treating these integrals but unfortunately the programs are still very consuming of computer time. These integrals have never appeared in quantum chemistry before and we had to develop new methods of doing them. We do not believe our methods are presently optimum. Big savings in computer time can probably be achieved with a few years more efforts ("years" may seem long but not when one considers the thirty or so years it took to reach the state of the art in present molecular programs). Our strategic problem was that it was senseless to develop speedy packages to use in a method that might not work. Hence we used our slow packages and went on to the second problem, that of parametrizing the effective potential. In a sense the problems are linked, in that the trial and error fittings necessary to parametrize are severely limited in application by the computer cost for doing integrals as parameters are varied. The

second problem is therefore a so far less than ideal but perhaps not unacceptable fit of the parameters in the effective potential to the known curves. We will return to this problem in section 4. IV.

Now of the outset of our work we decided that we would like as input from theory some accurate GaKr curves so that we could get on effective potential for Kr to use in InKr or TlKr computations. Hence we split our work in three parts - the first part reviewed in §2 was to do accurate CI calculations on GaKr.

§3 is an application of the Gordon-Kim method to GaKr and a comparison with the results from §2.

The third part was to develop and test our theory in §4. As it turned out the third part is still not able to take advantage of the first part since even for Li-He we have not, because of the above two mentioned problems, achieved success. In any case we will report here our progress omitting the large sections of efforts that lead to even inferior methods of integration and parametrization and reporting only the most promising methods. At the writing of this report we are close to a critical test calculation of LiHe, having achieved what may be a satisfactory (how satisfactory it is future results will show) calculation of the effective Helium potential. Time and personnel changes have prevented us from making this last step which we shall certainly do in the near future even without further support. If we are successful we shall return to the problems of speeding up our integral computation methods and routines. This will prepare the method to move on to bigger systems and get us to where we had hoped to be now, at the end of our contract period. Of course if the calculations are not successful theoretical

reasons need be sought and the promise of the method would be in question. While doing this work Dr. Taylor and Dr. Jung had a discussion about electron scattering in a strong laser field and wrote a paper about this subject. A copy is included in Appendix E. This work was not in the original grant but as many things in science it just happened in discussion. No computing funds from the grant were used for this project.

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Electronic States of GaKr : Ab initio calculations of a prototype for TlKr

2.1 Introduction

Among the metal-rare gas eximers, the TlXe system is believed to be an excellent candidate for an efficient visible, high power, tunable laser.¹ Since ab initio calculations on this system are beyond the scope of present computer programs, we present here a configuration interaction (CI) calculation on GaKr, which is the largest group IIIB-rare gas system for which CI calculations can be done. We use the calculated GaKr curves to model the potential curves for InKr and TlKr. Although our model does not allow further extrapolation from TlKr to TlXe, it is hoped that these calculations will yield some insight into the properties of the TlXe eximer. In addition, Gallagher² has recently raised the possibility of using GaXe as a laser if the Ga can be obtained from dissociation of GaI₃. Consequently the GaKr curves should also be of intrinsic interest.

In this paper, the CI calculations on GaKr are presented along with the model calculations on InKr and TlKr. These potential curves are used as the basis of a classical calculation of the emission and absorption coefficients for these systems.

2.II Details of the calculation

A. Basis set

The calculations use (14s11p6d) primitive Gaussian bases for gallium and krypton³ as a starting point. The core orbitals (1s,2s,2p,3s,3p) are singly contracted to the Hartree-Fock atomic orbitals while the valence orbitals (4s and 4p) and the 3d orbitals are each described by two contracted functions (see Table I). The resulting (5s4p2d/5s4p2d) contracted bases are constructed using the general contraction scheme of Raffenetti.⁴

These basis sets are extended to include polarisation by adding two diffuse s functions (5s and 5s') and a diffuse p function (5p) to describe the lowest Rydberg orbitals. The exponents for these orbitals ($\zeta(5s) = .026$, $\zeta(5s') = .011$, $\zeta(5p) = .01$) are obtained from atomic calculations on the excited states of Ga. The final basis set thus consists of a (16s12p6d) primitive basis contracted to [7s5p2d] for Ga and a (14s11p6d) primitive basis contracted to [5s4p2d] for Kr.

B. SCF calculation

The starting point for the CI calculation is a Hartree-Fock calculation on the $^2\Sigma^+$ state

$$. . . . 13\sigma^2 14\sigma^2 7\pi^4 15\sigma^2 16\sigma$$

The inner core molecular orbitals (twelve σ , twelve π and four δ) are held doubly occupied from this point on and are replaced by the rigorous nonlocal Hartree-Fock potential.

$$V_{\text{core}} = V_N + \sum_{i=\text{core}} (2J_i - K_i)$$

With the core orbitals removed from consideration, it is convenient to renumber the valence orbitals so that the Hartree-Fock configuration is written as

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 1\pi^4$$

At large R the correspondence for the valence orbitals is

$$1\sigma \rightarrow 4s_{\text{Kr}}$$

$$2\sigma \rightarrow 4p_{\text{Kr}}$$

$$3\sigma \rightarrow 4s_{\text{Ga}}$$

$$4\sigma \rightarrow 4p_{\text{Ga}}$$

$$1\pi \rightarrow 4p_{\text{Kr}}$$

In addition to the valence orbitals, nine σ , six π and four δ virtual orbitals are used in the CI calculations. The lowest virtual orbitals (5σ , 6σ , 7σ , 2π , 3π), which correspond to the Ga $5s$, $5s'$, $4p$ and $5p$ atomic orbitals for large internuclear separations, are obtained by the improved virtual orbital (IVO) procedure.⁵ The IVO orbitals are obtained by removing the electron from the 4σ (valence) orbital of the above configuration and calculating the virtual orbitals for the $(N-1)$ -electron Hamiltonian.

C. CI calculations

Full polarization CI (POL-CI) calculations⁶ which provide a balanced description of all states of the $4s$ - $4p$ manifold were carried out. A set of reference configurations was chosen (see Table II) to describe the dominant configurations for the $^2\Sigma^+$ and $^2\Pi$ states of the molecule and the $^1\Sigma^+$ state of the ion.

The full POL-CI calculations include all $(1+2)$ electron excitations relative to each reference configuration subject to the restrictions that no more than one electron occupy the Rydberg 5σ orbital and no more than one electron occupy any virtual orbital (6σ , 2π etc.). This results in 764 spatial and 2314 spin configurations for the $^2\Sigma^+$ states, 556 spatial and 1565 spin configurations for the $^2\Pi$ states and 368 spatial and 558 spin configurations for the $^1\Sigma$ state. A total of 15σ , 14π and 2δ occupied and virtual orbitals are used in the POL-CI calculations.

The potential energy curves (Fig. 2 and Table III) from the POL-CI calculations generally follow the behavior predicted from these theoretical considerations. These calculations are not, however, designed to treat long-range dispersion forces. Many excitations which contribute to a $C_6 r^{-6}$ attraction are not included in the wavefunction. For these reasons, one would expect deeper wells in all the potential curves including the two lowest, generally repulsive, states. As predicted, the 1^2_{Π} state is less repulsive than the $1^2_{\Sigma^+}$ state. The bound excited state $2^2_{\Sigma^+}$ has a minima at 6.36 a.u. about 3.0 eV above the ground state curve, while the minima in the ion curve is at 6.28 a.u. and 5.6 eV above the ground state. The well depths are compared with those obtained by Gallagher¹¹ in Table IV, and as expected, Gallagher's wells are deeper.

The dipole moments of these states and the transition moments between $2^2_{\Sigma^+}$ and the lower states have also been calculated and are given in Table V and Figs. 3 and 4.

B. Electronic states including spin-orbit coupling

A complete treatment of the electronic states of GaKr must include the effects of spin-orbit coupling. The states considered here, which dissociate to the closed-shell ground state of Kr and an open-shell state of Ga or Ga^+ are influenced only by the spin-orbit matrix elements of the open-shell atom.

Following the procedure used previously,^{7,8,9,10} we have adopted a simple model for including the effects of spin-orbit coupling on the calculated potential energy curves and wavefunctions. The experimental spin-orbit parameters for the open-shell atom (Ga and later In, Tl) are used to determine the matrix elements of the spin-orbit interaction, H_{so} , coupling the molecular states at infinite separation and these matrix elements are assumed to be independent of internuclear distance. The resulting spin-orbit matrix H_{so} is added to the diagonal matrix of electronic energies $H_{elec}(R) = \delta_{ij}E_i(R)$:

$$H(R) = H_{elec}(R) + H_{so}$$

and the total matrix H is then diagonalized at each internuclear distance R . Thus, in addition to the assumption that the spin-orbit matrix elements do not change as functions of R , this model assumes that only one-center terms need be included so that only the spin-orbit coupling on Ga is important. We would expect this procedure to provide reasonable results to the extent that the molecular states retain the identity of the atomic

states from which they are formed. The spin-orbit matrices are given in Table VI along with the atomic parameters used in these calculations. The parameter λ is chosen so that the atomic $^2p_{3/2}$ and $^2p_{1/2}$ states have energies of $+\lambda$ and -2λ respectively.

We shall label the molecular states using the convention of Hund's case (c) where Ω , the projection of total angular momentum along the molecular axis, is the only good quantum number. Ω is defined as $\Omega = L + S_z$, where L and S_z are the orbital and spin angular momentum projection, respectively. The molecular $^2\Sigma^+$ states have only a $\Omega = 1/2$ component, while the $^2\Pi$ states yield a $\Omega = 3/2$ and $\Omega = 1/2$ state. The states in the Ω representation are labeled according to increasing energy by a Roman numeral. So the $\Omega = 1/2$ states are designated as I 1/2, II 1/2 and the $\Omega = 3/2$ states are I 3/2, II 3/2.

The coupled states are expressed as follows:

$$\begin{aligned} |I\ 1/2\rangle &= C_\Sigma |1^2\Sigma^+\rangle + C_\Pi |1^2\Pi\rangle \\ |II\ 1/2\rangle &= -C_\Pi |1^2\Sigma^+\rangle + C_\Sigma |1^2\Pi\rangle \\ |I\ 3/2\rangle &= |1^2\Pi\rangle \end{aligned}$$

The spin-orbit coefficient C_Σ and C_Π are given in Table VII. The potential curves and transition moments for GaKr including spin-orbit coupling are given in Table VIII and Figs. 5 and 6.

2.IV Extrapolations to InKr and TlKr

The potential curves for InKr and TlKr are modeled on the GaKr curves. The lowest excitation energies and the ionization potentials for the series Ga, In, Tl are given in Table IX. As can be seen, this series does not form a steady progression. In has a lower ionization potential and lower excitation energies than Ga, as expected for a heavier atom. However, Tl has a higher ionization potential and higher excitation energies. This is due in part to the presence of a filled 4f shell in Tl and the larger spin-orbit effects.¹² These effects should be considered when extrapolating the GaKr curves to InKr and TlKr.

To simulate InKr and TlKr, the experimental spin-orbit parameters for In and Tl are used to couple the GaKr curves. The curves are also shifted to give the correct atomic excitation energies at $R = \infty$ (see Table IX). This procedure should give at best a qualitative description of states of InKr and TlKr, since the non-spin-orbit coupled states are expected to have quantitatively different well depths and equilibrium separations.

The effect of the increasing spin-orbit perturbation in going from Ga to In and Tl is evident in the calculated curves which are given in Figs. 7 and 8. Only the well depths and positions for the $I 1/2$ and $II 1/2$ states are affected by the spin-orbit coupling. The other states

are the same as those for GaKr except that they have the correct asymptotic spacing.

The mixing parameters from the spin-orbit coupling calculations for TlKr are also used as the coefficients of the GaKr wave function to estimate the transition moments for this system. The TlKr transition moments are given in Table X and Fig. 9.

2.V Absorption and stimulated emission coefficients for possible laser transitions

The interest in the group IIIB-rare gas systems arises from the possibility of their use as visible laser systems. In order to judge their usefulness as lasers it is convenient to calculate the absorption $k_v(t)$ and stimulated emission $g_v(T)$ coefficients. Obtaining quantum-mechanical results for these quantities would require a complex calculation which would be inconsistent with the extrapolations used to obtain the InKr and TlKr curves. Consequently, we have used Gallagher's analysis [17], which is based on the classical Frank-Condon principle.

In order to obtain g_v and k_v , the CI curves are first fit by Morse potentials. The parameters for these Morse potentials are given in Table XI. These parameters can then be used in Gallagher's equations, along with the atomic transition rate, to obtain absorption and stimulated emission coefficients for pressure and excitation conditions of interest to experimentalists. We have calculated these coefficients for two different types of conditions. The high temperature results correspond to the case where the concentration of the metal is obtained from the vapor pressure of the metal itself, while the low temperature results correspond to obtaining the required concentration of the metal from vaporization of MI_3 ($M = Ga, In, or Tl$). This latter condition has been suggested by Gallagher as a possible means of obtaining high concentrations of the metal at low temperatures. In both cases the densities used are $10^{20}/cm^3$ for Kr, $10^{16}/cm^3 = 3[M^2P_{1/2}] = 1.5[M^2P_{3/2}]$ and $2 \times 10^{14}/cm^3 = [M^2S_{1/2}]$. The resulting absorption and stimulated

emission coefficients for GaKr , InKr and TlKr are given in Figures 10 to 15.

A paper has been published about the work presented in §2.
See Appendix A.

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Table I. Gaussian exponents and contraction coefficients

Exponents		Contraction coefficients				
Gallium atom						
	1s	2s	3s	4s	4s'	
457600.	.000222	-.000069	.000026	-.000006		0.0
68470.	.001732	-.000535	.000205	-.000048		0.0
15590.	.008952	-.002814	.001070	-.000247		0.0
4450.	.035874	-.011275	.004337	-.001007		0.0
1472.	.114000	-.038495	.014707	-.003399		0.0
541.3	.274138	-.100714	.039748	-.009279		0.0
214.8	.414793	-.211832	.084475	-.019587		0.0
88.81	.275395	-.175448	.079654	-.019104		0.0
27.18	.029561	.479840	-.291821	.072753		0.0
11.54	-.006815	.634145	-.527118	.134137		0.0
3.303	.002253	.069592	.583707	-.181778		0.0
1.334	-.001017	-.012299	.674103	-.358241		0.0
.1947	.000251	.002774	.028077	.615164		0.0
.07158	0.0	0.0	0.0	0.0		1.0
	5s	5s'				
.026	1.0	0.0				
.011	0.0	1.0				
	2p	3p	4p	4p'	5p	
3274.	.001513	-.000576	.000094	0.0	0.0	
765.4	.013070	-.004981	.000800	0.0	0.0	
241.6	.067263	-.026421	.004337	0.0	0.0	
89.39	.219542	-.089529	.014443	0.0	0.0	
36.36	.421107	-.186734	.031377	0.0	0.0	
15.60	.376515	-.144494	.021501	0.0	0.0	
6.472	.089425	.258956	-.046233	0.0	0.0	
2.748	-.000502	.570187	-.125293	0.0	0.0	
1.090	.001761	.325305	-.045636	0.0	0.0	
.2202	-.000247	.016563	.452811	0.0	0.0	
.06130	0.0	0.0	0.0	1.0	0.0	
.01	0.0	0.0	0.0	0.0	1.0	
	3d	4d				
59.66	.031949	0.0				
17.10	.163546	0.0				
6.030	.367457	0.0				
2.171	.456851	0.0				
.6844	.305161	0.0				
.160	0.0	1.0				

Table I. Gaussian exponents and contraction coefficients

Exponents	Contraction coefficients				
	Krypton atom				
	1s	2s	3s	4s	4s'
605700.	.000231	-.000073	.000029	-.000009	0.0
90300.	.001755	-.000551	.000221	-.000070	0.0
20920.	.009076	-.002894	.001159	-.000369	0.0
5889.	.036990	-.011834	.004781	-.001522	0.0
1950.	.116154	-.039826	.016056	-.005118	0.0
718.2	.278401	-.104801	.043454	-.013886	0.0
285.4	.415746	-.217093	.091899	-.029537	0.0
118.6	.267204	-.175562	.083789	-.027309	0.0
38.16	.027870	.471395	-.303023	.103498	0.0
16.45	-.005998	.636794	-.570620	.208810	0.0
5.211	.002217	.082255	.501751	-.235737	0.0
2.291	-.001092	-.014138	.760483	-.553570	0.0
.4837	.000306	.003289	.044857	.701123	0.0
.1855	0.0	0.0	0.0	0.0	1.0
	2p	3p	4p	4p'	
4678.	.001392	-.000569	.000156	0.0	
1120.	.011666	-.004777	.001286	0.0	
357.1	.060858	-.025631	.007059	0.0	
131.4	.210040	-.092159	.024990	0.0	
52.86	.421000	-.200936	.056870	0.0	
22.70	.383515	-.160784	.040225	0.0	
9.547	.097383	.267789	-.084756	0.0	
4.167	-.001087	.585908	-.240291	0.0	
1.811	.002209	.291397	-.038636	0.0	
.5337	-.000509	.015484	.599154	0.0	
.1654	0.0	0.0	0.0	1.0	
	3d	4d			
125.6	.019168	0.0			
33.31	.125638	0.0			
12.15	.366069	0.0			
4.350	.502482	0.0			
1.494	.264377	0.0			
.35	0.0	1.0			

Table II. Reference Configurations

2_{Σ}^{+} states

1	$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 1\pi^4$
2	$1\sigma^2 2\sigma^2 3\sigma^2 5\sigma 1\pi^4$
3	$1\sigma^2 2\sigma^2 3\sigma^2 6\sigma 1\pi^4$

2_{Π} states

1	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 2\pi$
2	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 3\pi$

1_{Σ}^{+} state (GaKr^{+})

1	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$
---	--

Table III. POL-CI calculations on the low-lying states of GaKr and the ground state of GaKr⁺. All energies are relative to -4674. hartrees.

R	$1^2\Sigma^+$	$2^2\Sigma^+$	$1^2\Pi$	$1^1\Sigma^+$
∞	-1.200042	-1.095050	-1.198917	-0.992860
15.00	-1.200121	-1.095025	-1.198978	-0.993044
10.00	-1.200290	-1.094061	-1.199328	-0.994018
8.00	-1.198650	-1.094202	-1.200204	-0.996703
7.00	-1.193963	-1.095454	-1.200450	-0.999505
6.00	-1.179381	-1.096768	-1.197718	-1.002018
5.00	-1.135164	-1.088552	-1.179245	-0.992868
4.50	-1.086883	-1.064404	-1.148099	-0.967583
4.00	-1.018697	-0.992381	-1.079327	-0.906827
3.75	-0.968656	-0.933786	-1.025394	-0.856247

Table IV. Potential well depths

Mole - cule	State	CI		Morse Fit		Gallagher	
		R	$\Delta E(\text{eV})$	R	$\Delta E(\text{eV})$	R	$\Delta E(\text{eV})$
GaKr	$I_{1/2}(X_{1/2})$		$\sim .018$	7.55	.021		
	$I_{3/2}(X_{3/2})$		$\sim .040$	7.18	.040		
	$II_{1/2}(A_{1/2})$	~ 10	.006	10.15	.00642		
	$III_{1/2}(B^2\Sigma_{1/2})$	6.36	.064	6.26	.080		
GaKr ⁺	I_0	6.28	.26	5.95	.252		
InKr	$I_{1/2}$	~ 8	$\sim .013$	7.86	.00778		
	$I_{3/2}^a$						
	$II_{1/2}$	~ 10	$\sim .006$	9.98	.0064		
	$III_{1/2}^a$						
	I_0^a						
TlKr	$I_{1/2}$	~ 8	$\sim .010$	8.5	.012	7.01	.024
	$I_{3/2}^a$					6.58	.062
	$II_{1/2}$	~ 10	$\sim .006$	9.88	.064		
	$III_{1/2}^a$					6.09	.107
	I_0^a						

^a same as GaKr

Table V. Dipole and transition moments for the low-lying states of GaKr

R	χ^2_{Π}	$1^2\Sigma^+$	$2^2\Sigma^+$	$1^2\Sigma^+-\chi^2_{\Pi}$	$2^2\Sigma^+-\chi^2_{\Pi}$	$2^2\Sigma^+-1^2\Sigma^+$
15.00	0.00598	0.00156	0.07558	0.00183	-1.29167	-1.31011
10.00	0.02605	0.02048	0.56872	0.01631	-1.28976	-1.29762
8.00	0.09152	0.14168	0.89914	0.04761	-1.27767	-1.23098
7.00	0.18861	0.30443	0.95672	0.07894	-1.26770	-1.19024
6.00	0.41543	0.62092	0.81671	0.11663	-1.25536	-1.18926
5.00	0.90382	1.20144	0.45889	0.09916	-1.23487	-1.44020
4.50	1.24437	0.96841	1.19373	-0.13653	-1.20897	-2.06755
4.00	1.64453	-1.27575	5.47300	-0.84619	-0.86801	- .30554
3.75	1.88349	-1.13125	6.45764	-0.90367	-0.78769	.40946

Table VI. Quantities for spin-orbit matrices

$\Omega = 1/2$	2_{Σ^+}	2_{Π}	$\Omega = 3/2$	2_{Π}
2_{Σ^+}	0	$\sqrt{2} \lambda$	2_{Π}	$+\lambda$
2_{Π}	$\sqrt{2} \lambda$	$-\lambda$		

Ga $\lambda = .001255$ au

In $\lambda = .00336$

Tl $\lambda = .011835$

Table VII. Spin-orbit coefficients for the $\Omega = 1/2$ states

	$R(a_0)$	C_{Σ}	C_{Π}
GaKr	3.75000	.99955	.02998
	4.00000	.99960	.02813
	4.50000	.99961	.02787
	5.00000	.99927	.03811
	6.00000	.99641	.08468
	7.00000	.98199	.18892
	8.00000	.93379	.35782
	10.00000	.82915	.55902
	15.00000	.81649	.57736
InKr	3.75000	.99704	.07690
	4.00000	.99738	.07238
	4.50000	.99742	.07175
	5.00000	.99534	.09644
	6.00000	.98063	.19588
	7.00000	.93712	.34900
	8.00000	.87677	.48091
	10.00000	.82132	.57047
	15.00000	.81649	.57736
TlKr	3.75000	.97505	.22197
	4.00000	.97731	.21180
	4.50000	.97763	.21034
	5.00000	.96502	.26219
	6.00000	.91737	.39803
	7.00000	.86679	.49867
	8.00000	.83612	.54854
	10.00000	.81788	.57540
	15.00000	.81649	.57736

Table VIII. Rydberg-valence transition moments in GaKr
(with spin-orbit corrections)

R	III 1/2 - I 1/2		III 1/2 - II 1/2		III 1/2 - I 3/2
	Z	(X,Y)	Z	(X,Y)	(X,Y)
15.00	-0.75641	0.74574	-1.06969	-0.52733	-0.91335
10.00	-0.72540	0.75618	-1.07592	-0.50983	-0.91200
8.00	-0.44047	0.84363	-1.14948	-0.32327	-0.90345
7.00	-0.22486	0.88026	-1.16880	-0.16935	-0.89640
6.00	-0.10071	0.88449	-1.18499	-0.07517	-0.88767
5.00	-0.05489	0.87255	-1.43915	-0.03328	-0.87318
4.50	-0.05762	0.85454	-2.06674	-0.02383	-0.85487
4.00	-0.00859	0.61353	-0.30542	-0.01727	-0.61378

Table IX. Atomic states of Ga , In , and Tl

State	Excitation Energy					
	Ga		In		Tl	
	cm ⁻¹	eV	cm ⁻¹	eV	cm ⁻¹	eV
² P _{1/2}	0.0	0.0	0.0	0.0	0.0	0.0
² P _{3/2}	826.24	.10241	2212.56	.274228	7792.7	.965840
¹ S _{1/2}	24788.58	3.07234	24372.87	3.020814	26477.5	3.281665
I.P.	48380.	5.9963	46669.93	5.784348	49264.2	6.105886

Table X. Rydberg-to-valence transition moments in model TIKr
(with spin-orbit corrections)

R	III 1/2 - I 1/2		III 1/2 - II 1/2		III 1/2 - I 3/2
	Z	(X,Y)	Z	(X,Y)	(X,Y)
15.00	-0.75641	0.74574	-1.06969	-0.52733	-0.91335
10.00	-0.74665	0.74590	-1.06130	-0.52476	-0.91200
8.00	-0.67524	0.75539	-1.02925	-0.49558	-0.90345
7.00	-0.59354	0.77699	-1.03169	-0.44701	-0.89640
6.00	-0.47336	0.81433	-1.09099	-0.35332	-0.88767
5.00	-0.37761	0.84264	-1.38982	-0.22894	-0.87318
4.50	-0.43489	0.83575	-2.02130	-0.17981	-0.85487
4.00	-0.06471	0.59985	-0.29861	-0.13000	-0.61378

Table XI. Morse fitting parameters:

$$V(R) - V(\infty) = D_e[u^2 - 2u] \text{ where } u = \exp [B(R_e - R)]$$

Molecule	State	D_e	$R_e(a_0)$	$B(a_0^{-1})$
GaKr	I _{1/2}	.000772	7.56	.724
	I _{3/2}	.00147	7.19	.722
	II _{1/2}	.000625	10.14	.471
	III _{1/2}	.00295	6.26	.853
InKr	I _{1/2}	.000286	7.86	.817
	I _{3/2} ^a			
	II _{1/2}	.000474	10.24	.483
	III _{1/2} ^a			
TlKr	I _{1/2}	.00439	8.52	.633
	I _{3/2} ^a			
	II _{1/2}	.000408	10.12	.502
	III _{1/2} ^a			

^aSame as for GaKr

Fig. 1. Orbital diagrams for the electronic states of $\text{Ga} + \text{Kr}$ and $\text{Ga}^+ + \text{Kr}$. The lobes and circles represent the in-plane and out-of-plane p orbitals; the dashed circle denotes the Rydberg orbital.

THE LOW-LYING ELECTRONIC STATES OF GaKr AND GaKr^+

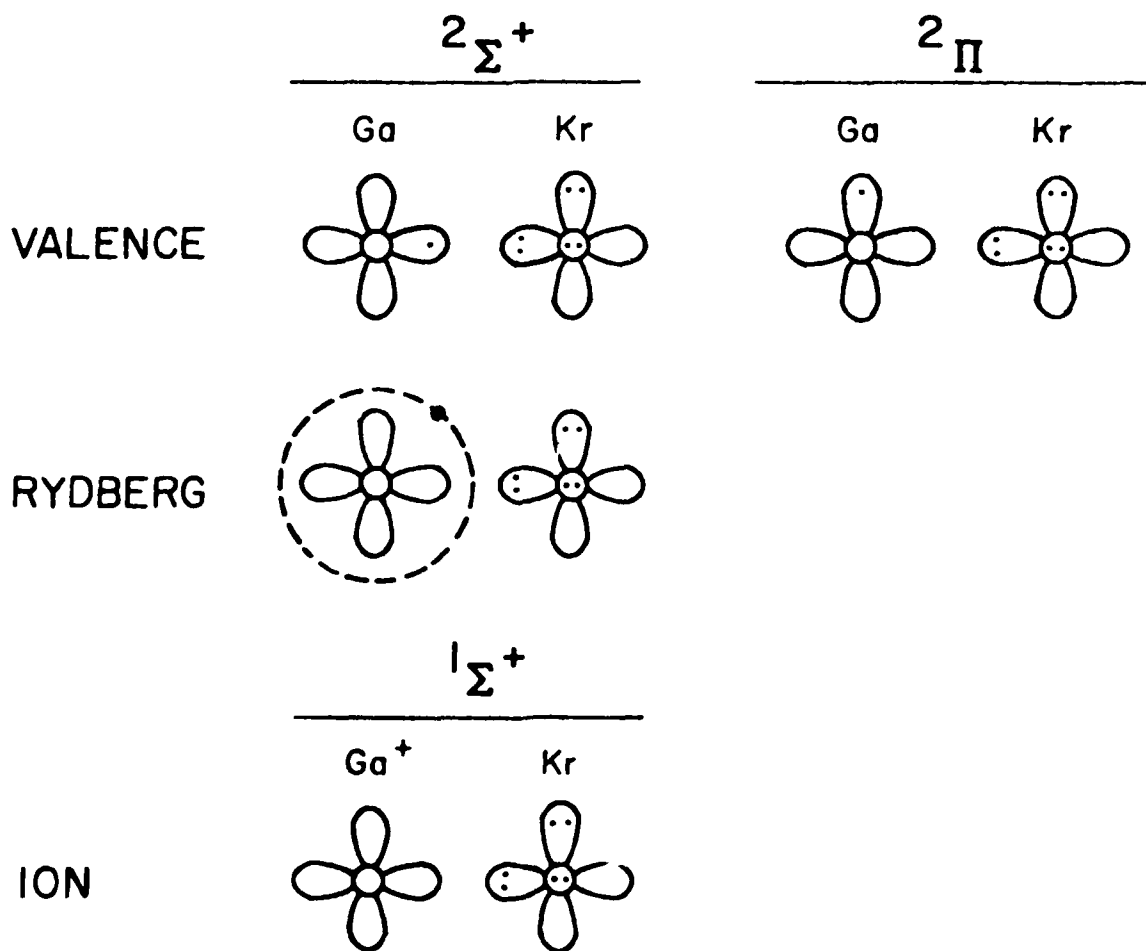


Figure 2.

THE LOW-LYING STATES OF GaKr AND GaKr^+

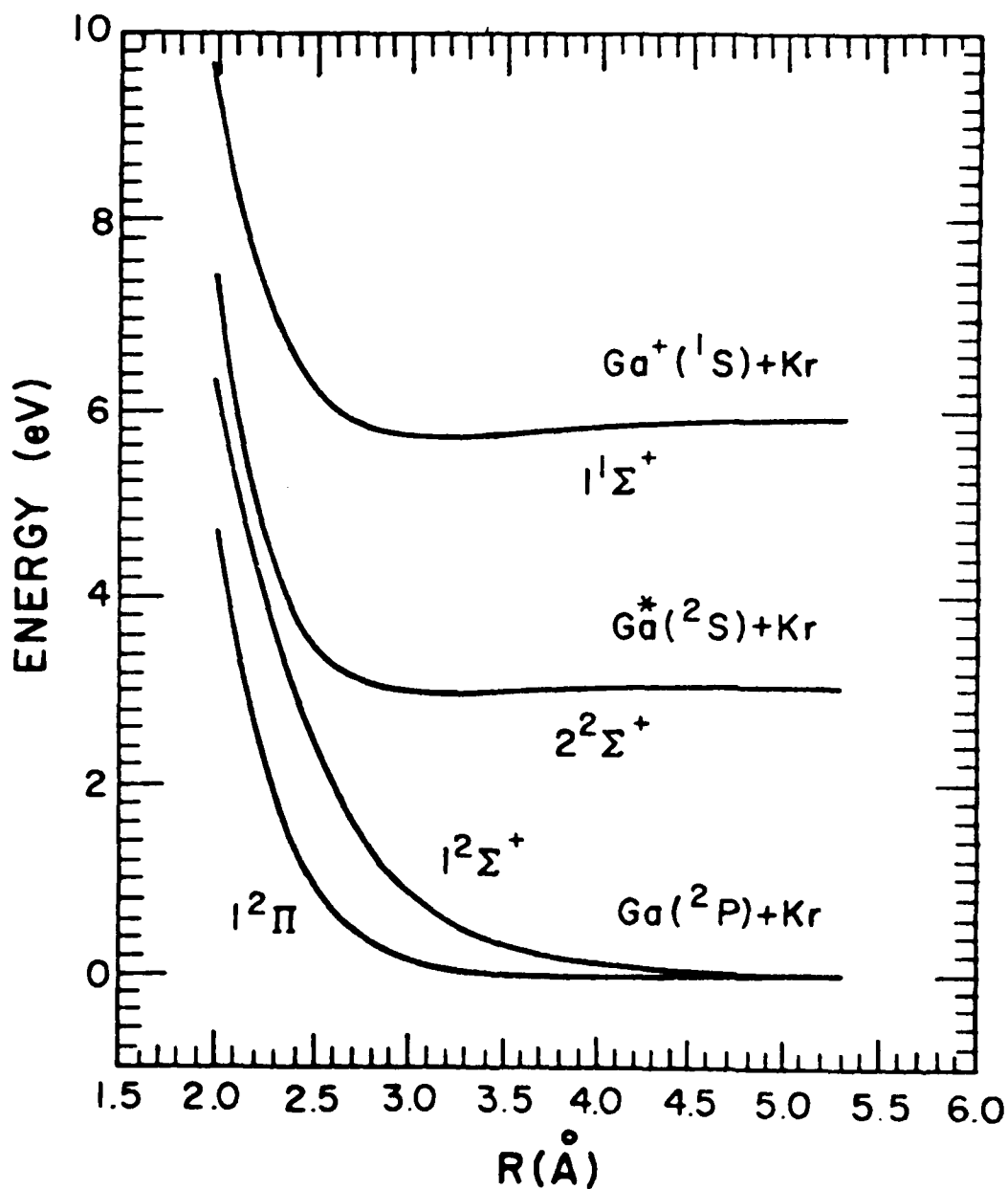


Figure 3.

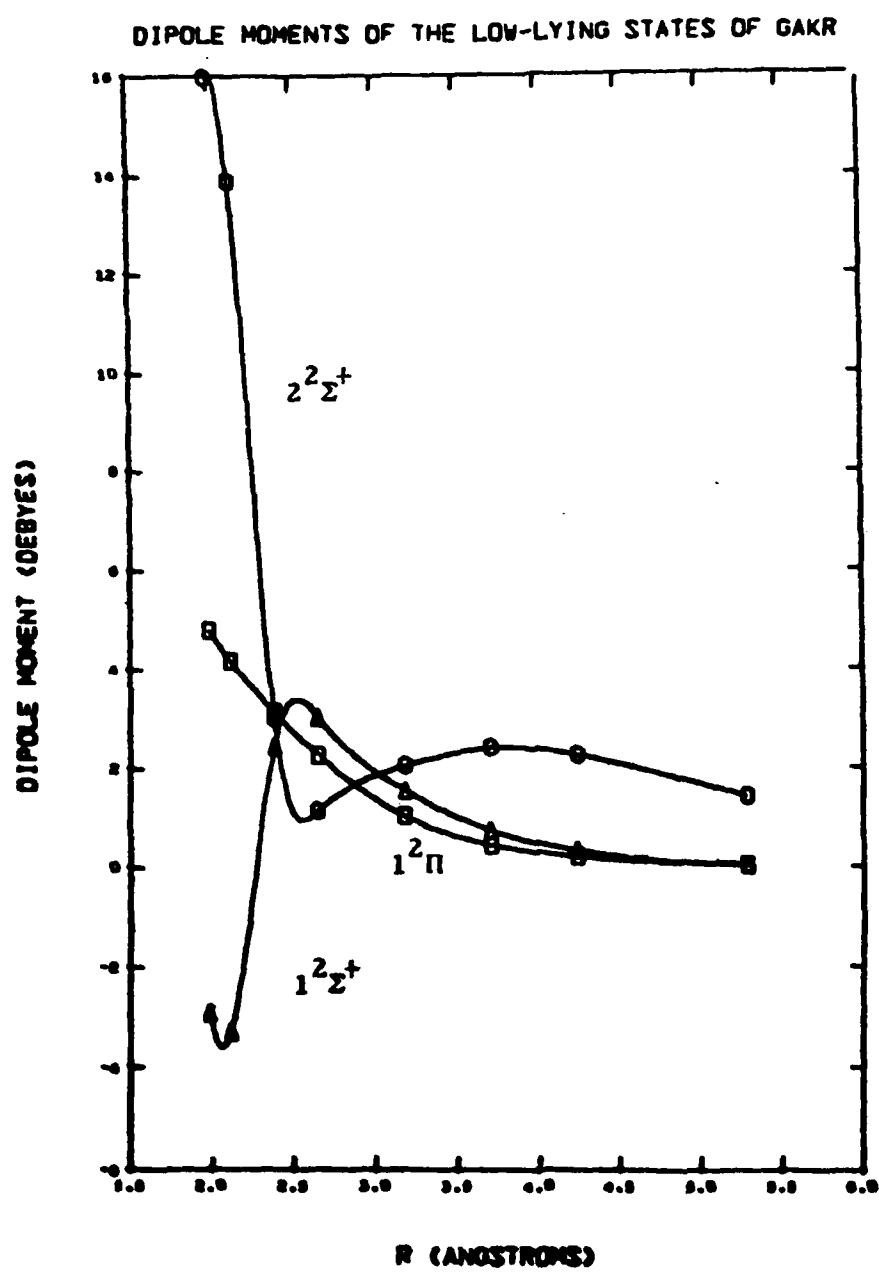


Figure 4.

DIPOLE TRANSITION MOMENTS AMONG
THE LOW-LYING STATES OF GaKr

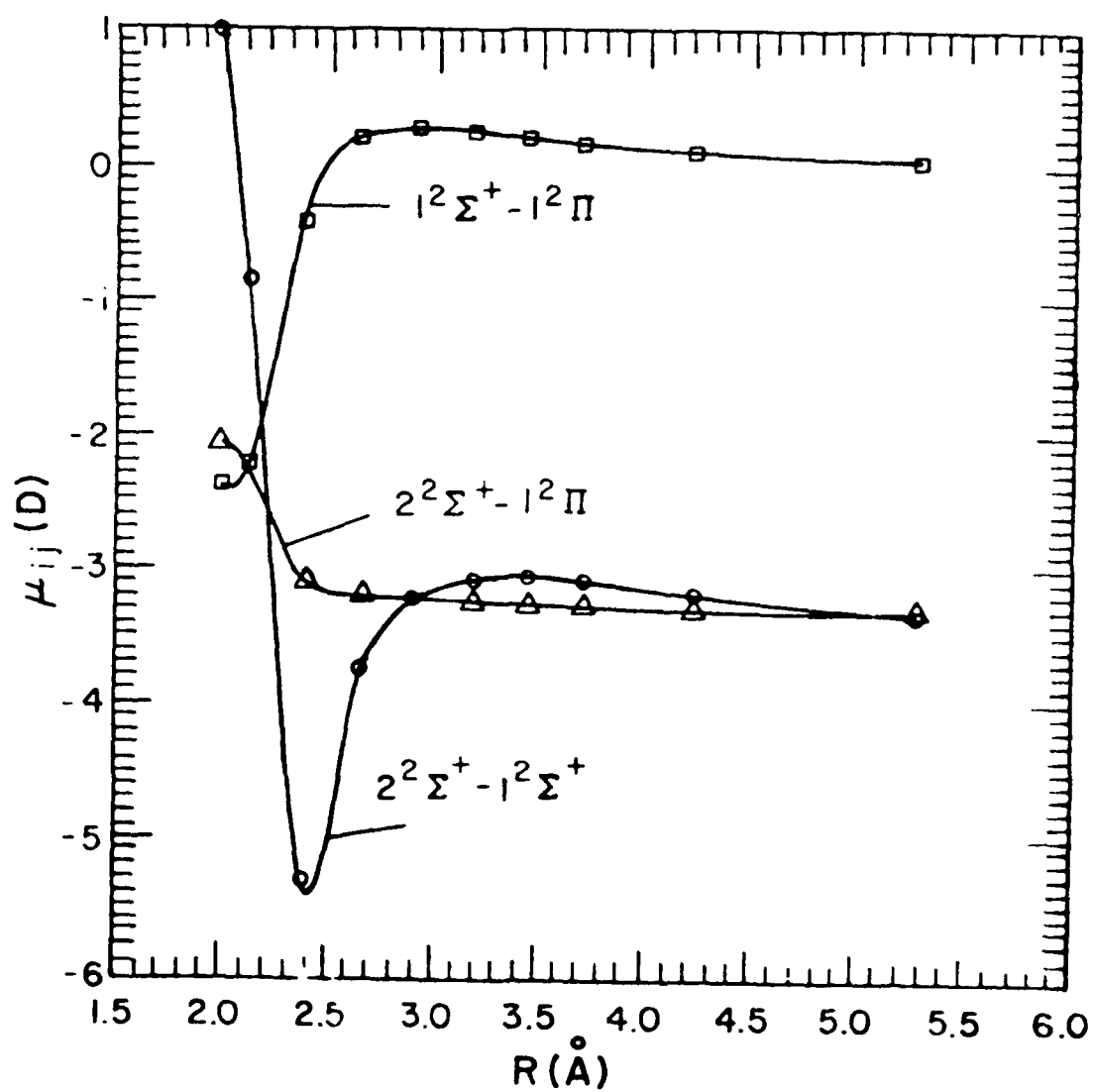


Figure 5.

THE LOW-LYING STATES OF GaKr AND GaKr⁺ WITH SPIN-ORBIT CORRECTIONS

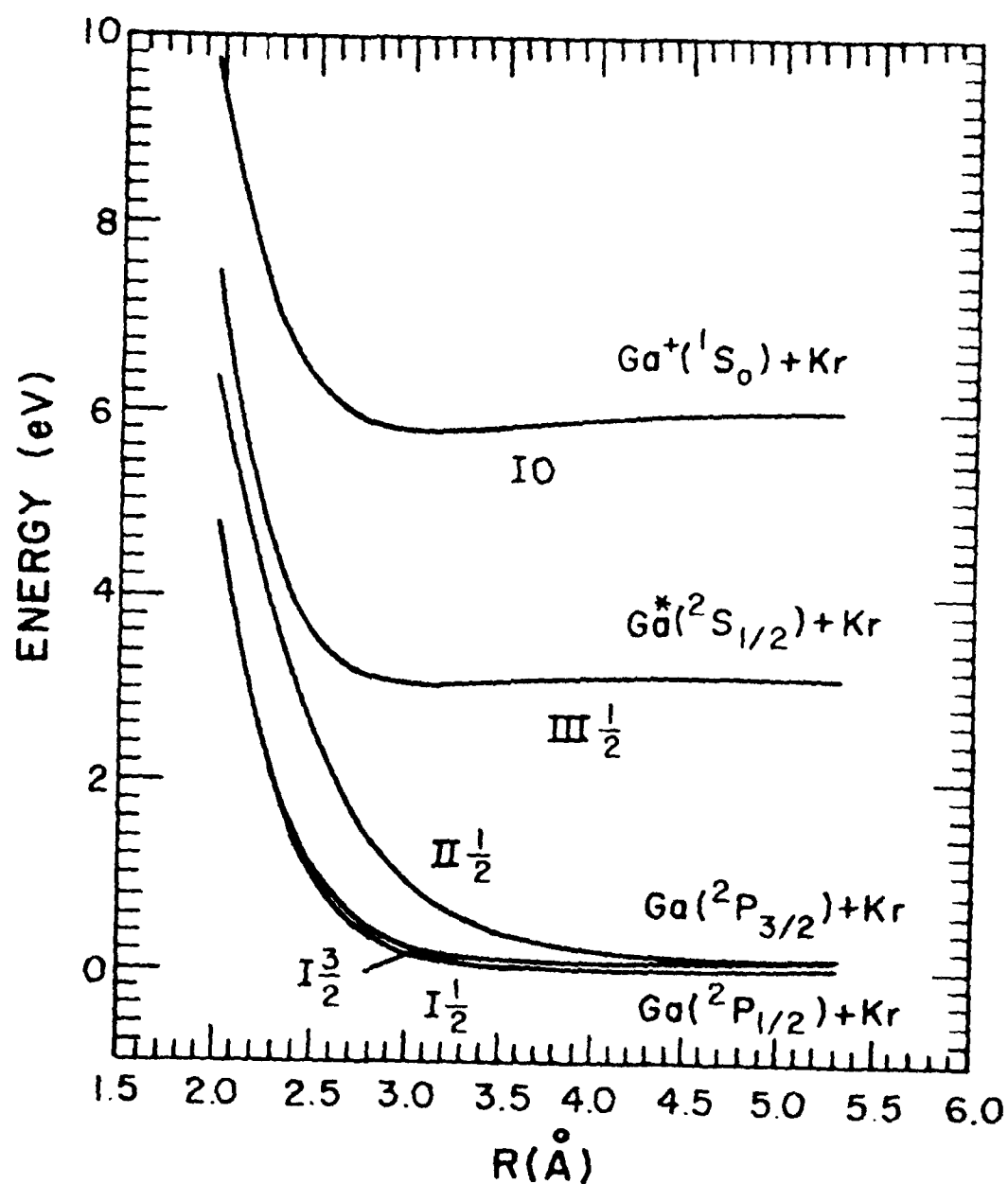


Figure 6.

DIPOLE TRANSITION MOMENTS AMONG
THE LOW-LYING STATES OF GaKr WITH
SPIN-ORBIT CORRECTIONS

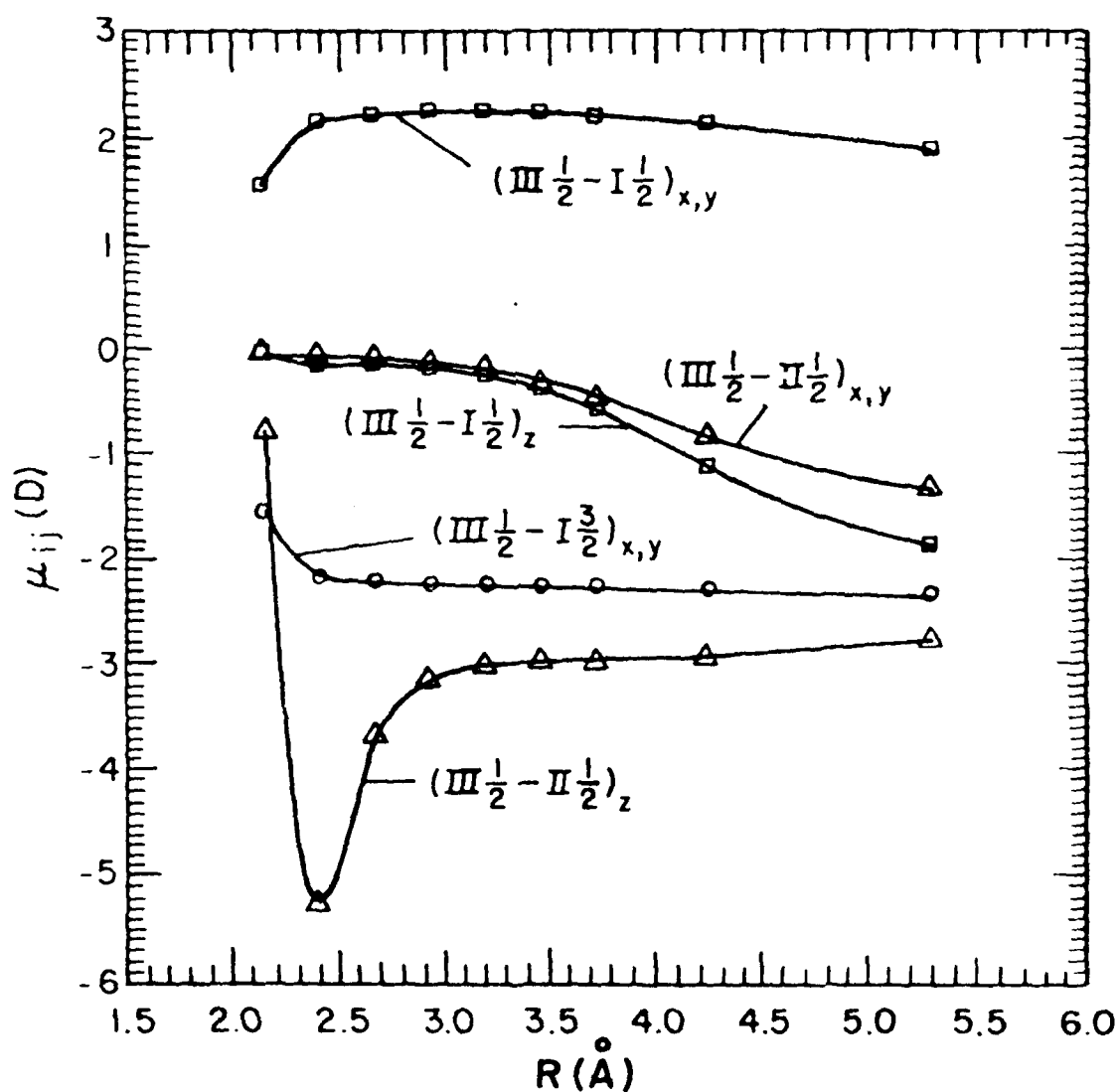


Figure 7.

THE LOW-LYING STATES OF InKr AND InKr⁺ WITH SPIN-ORBIT CORRECTIONS

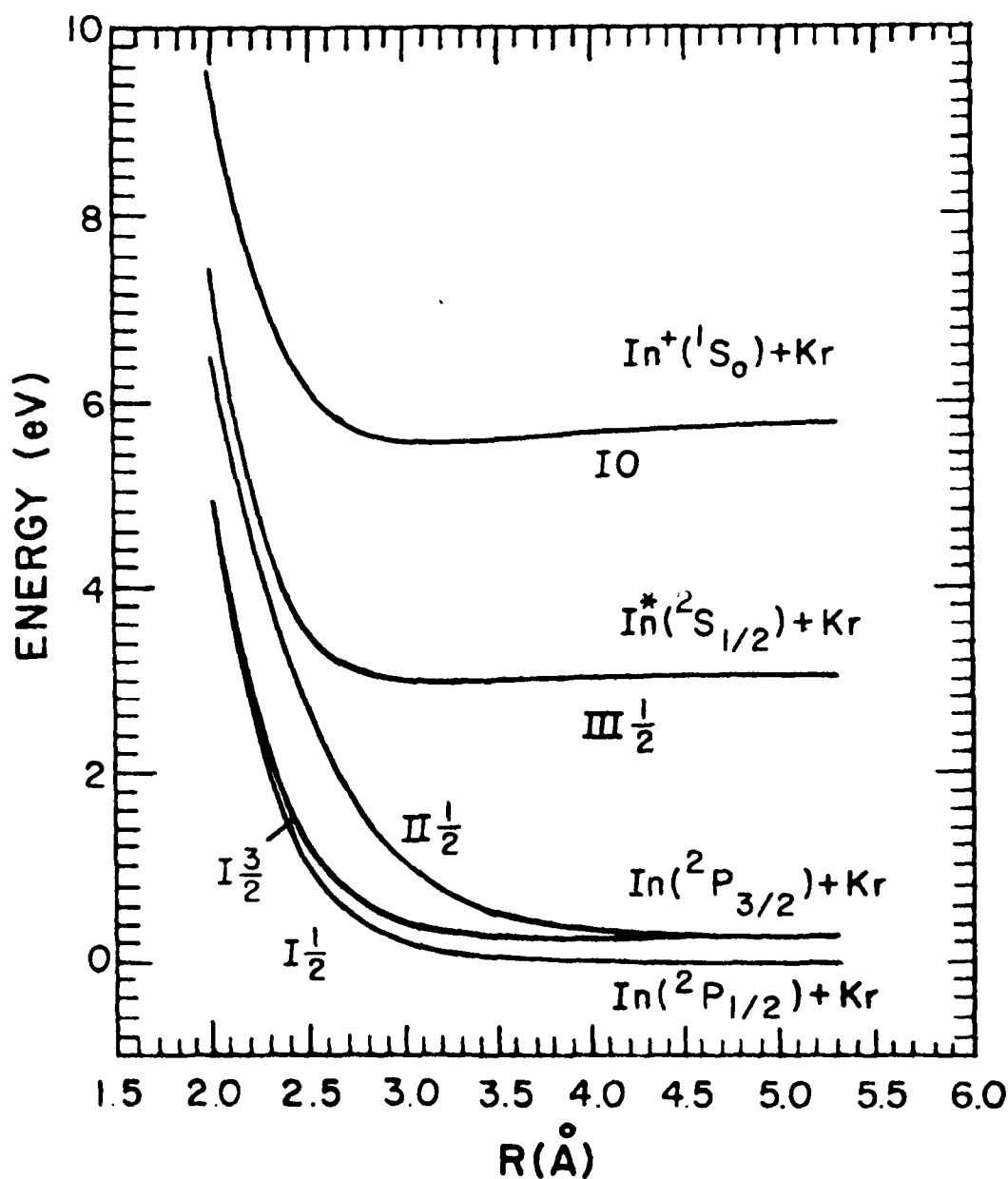


Figure 8.

THE LOW-LYING STATES OF TiKr AND TiKr^+ WITH SPIN-ORBIT CORRECTIONS

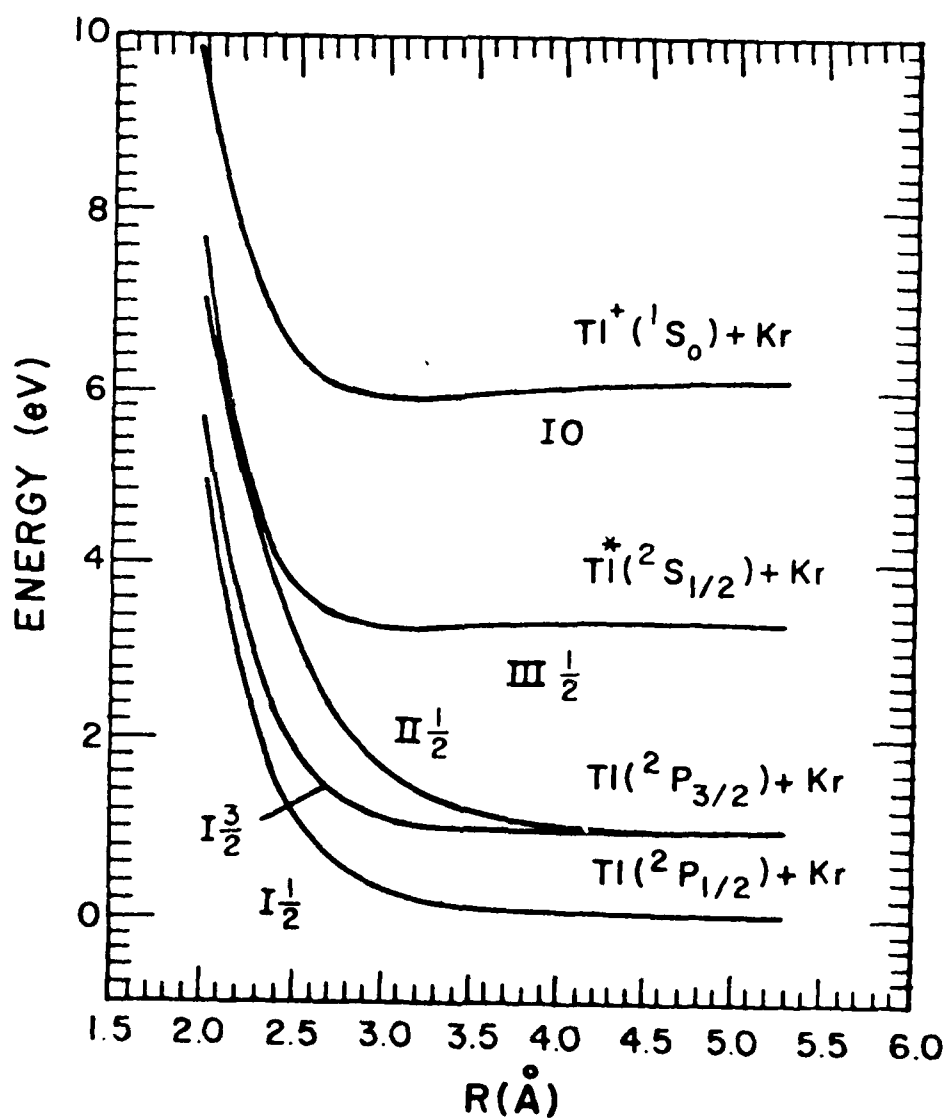


Figure 9.

DIPOLE TRANSITION MOMENTS CONNECTING
THE LOW-LYING STATES OF TiKr WITH
SPIN-ORBIT CORRECTIONS

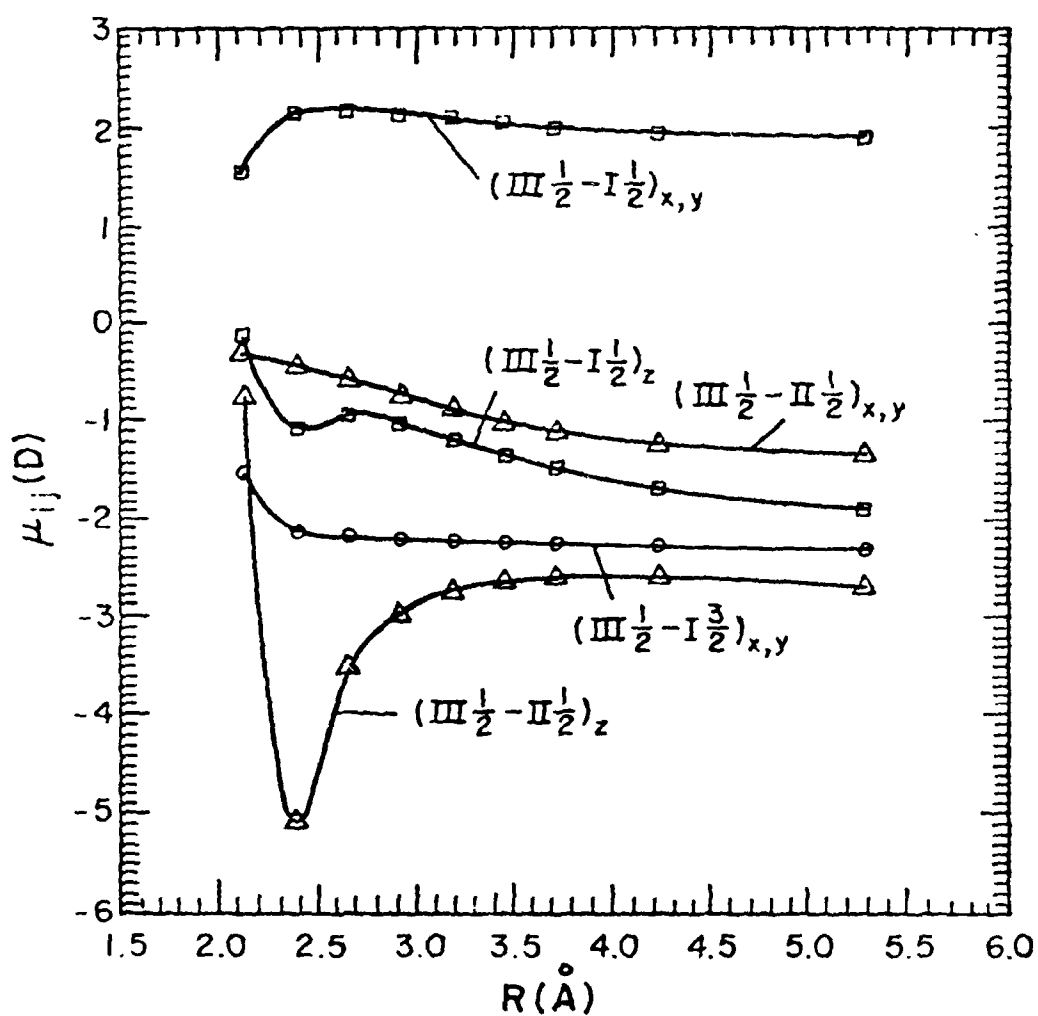


Figure 10.

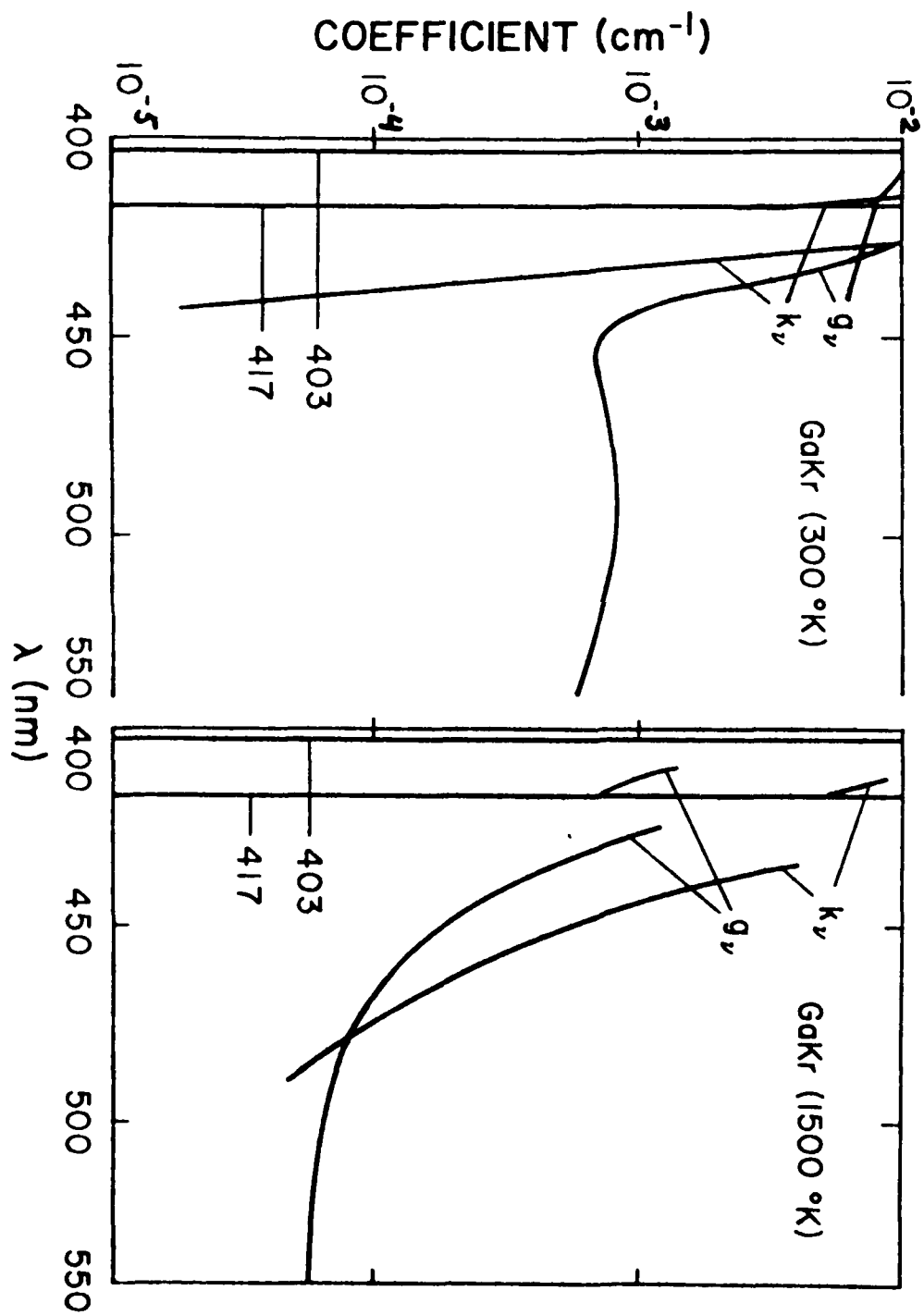


Figure 11.

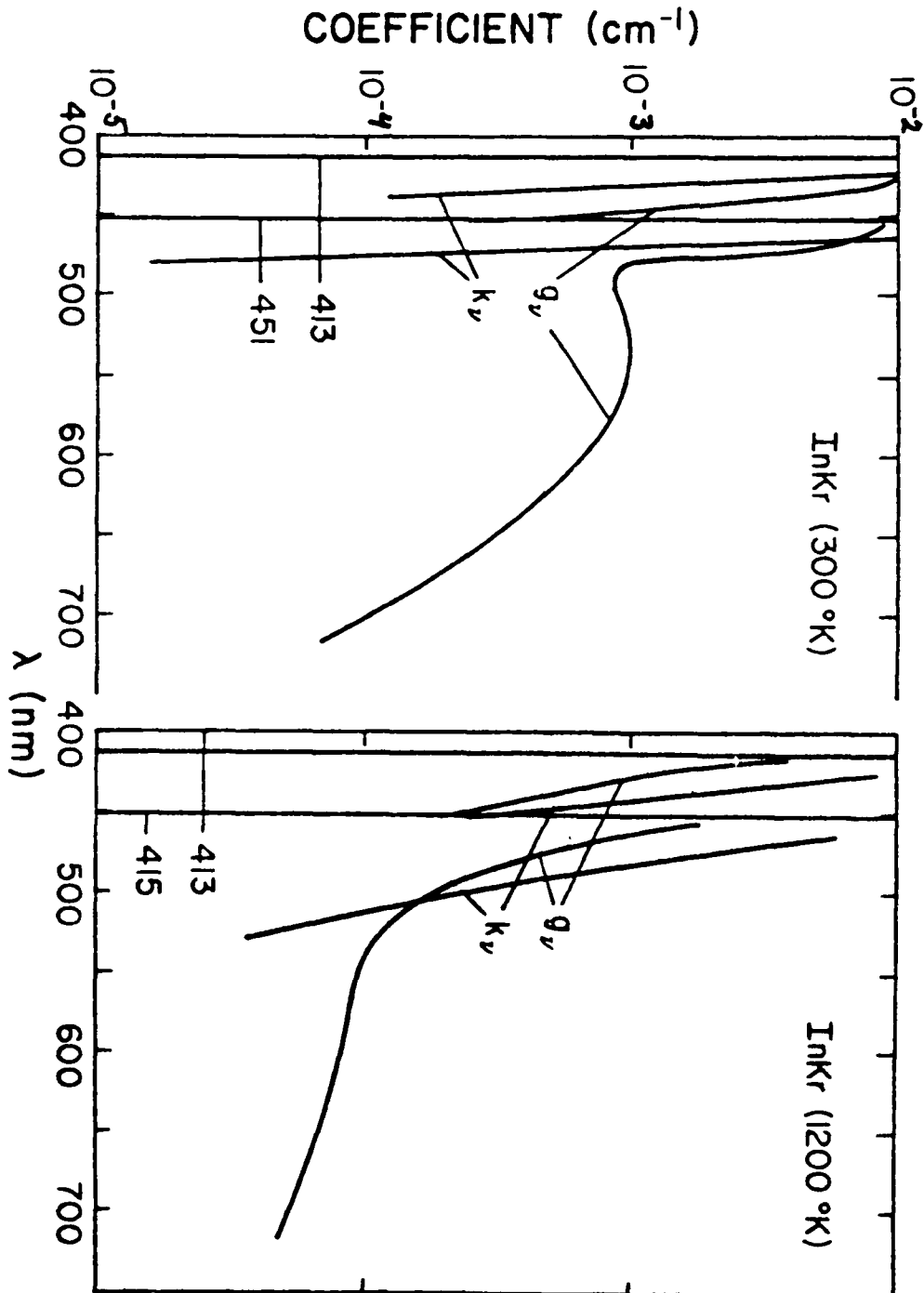
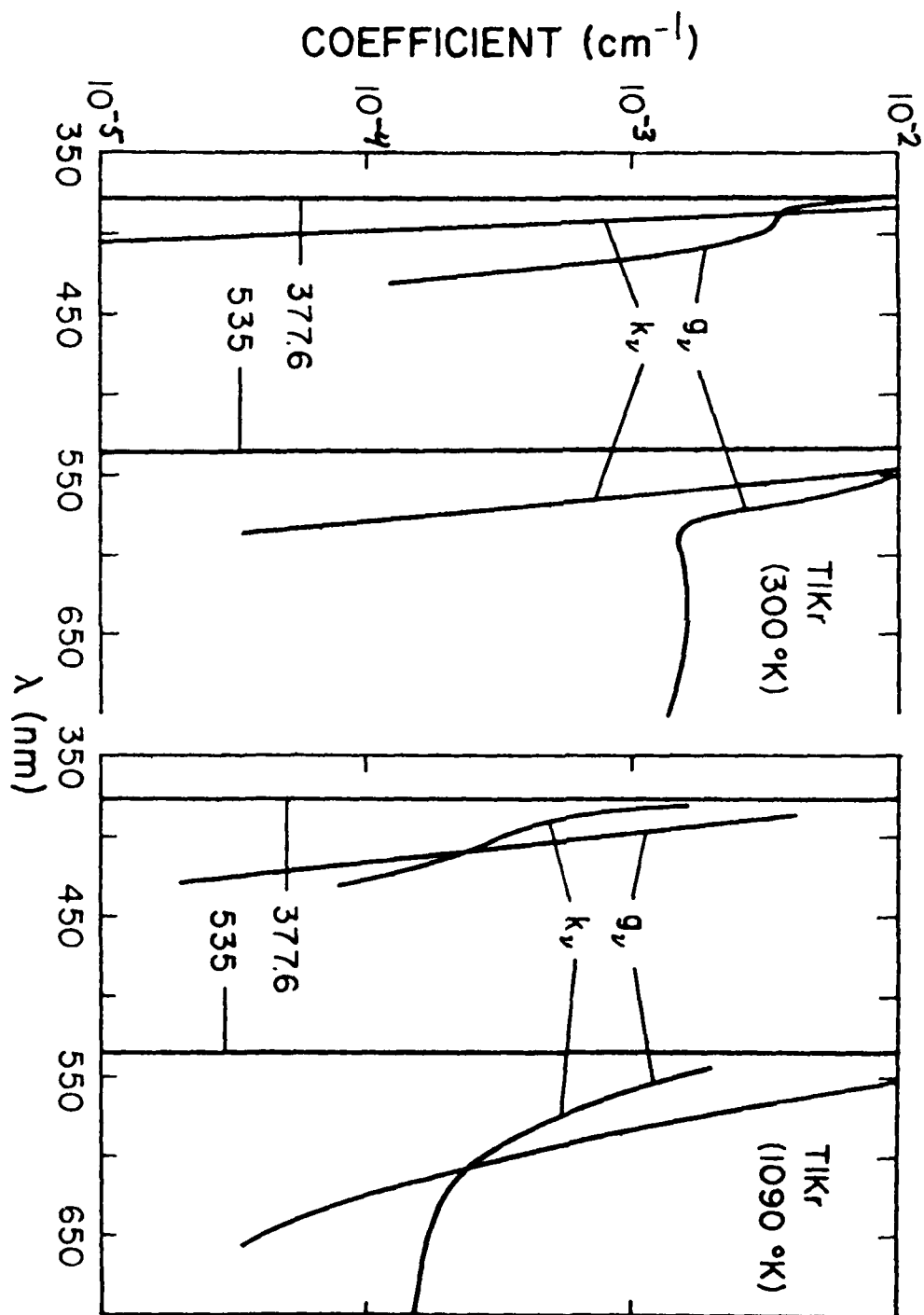


Figure 12.



Application of the Gordon-Kim theory to the group IIIB-rare gas systems.

In recent years, the electron gas methods developed by Gaydaenko and Nikulin [1], and Gordon and Kim [2] and modified by Rae [3] and Cohen and Pack [4] have proved successful in calculating the interaction energies of pairs of closed shell atoms or ions [1-5], of atom-molecule systems [6-7], of molecule-molecule systems [8], and, recently, of systems with one open shell atom [9]. These interaction energies are much more accurate than the simplicity of the Gordon-Kim (GK) method would lead one to expect.

The recent success of the GK method in calculating closed shell - open shell interaction energies has prompted us to use this method to calculate the interaction of group IIIB-noble gas pairs. The GK theory has been most successful in cases where the interaction is non-covalent and where the atoms are relatively undistorted. For these reasons, systems such as GaKr would seem to be ideal candidates for a GK calculation.

The electron-gas theory is briefly reviewed in part A, and our preliminary results on GaKr are given in part B.

A. The electron gas method

The method we have used is that of Gordon and Kim [2] as modified by Cohen and Pack [4]. A more detailed description of the theory is available in these two papers. Briefly the GK theory approximates the intermolecular

potential $V(R)$ at the distance R by

$$V(R) \approx V^{GK}(R) = V_{HF}^{GK}(R) + V_{corr}^{GK}(R)$$

where

$$V_{HF}^{GK} = V_k + V_c + V_e$$

and these three terms represent the kinetic, Coulomb and exchange interaction energies, respectively. To calculate these interaction energies, the electronic charge density ρ is approximated by the sum of the atomic charge densities,

$$\rho = \rho_a + \rho_b .$$

With this approximation, the Coulomb interaction can be calculated directly, but the other terms are all estimated by the formulas for the energy density of a uniform electron gas [4]. An additional modification [3,4] is made to the exchange energy to avoid self-exchange contributions.

B. Calculations

We have modified the molecule-molecule GK interaction program of Parker, Snow and Pack [8], which allows for non-spherical potentials, to calculate interaction energies for closed shell - open shell atomic pairs. The density of the open shell atom, in this case Ga, is divided into

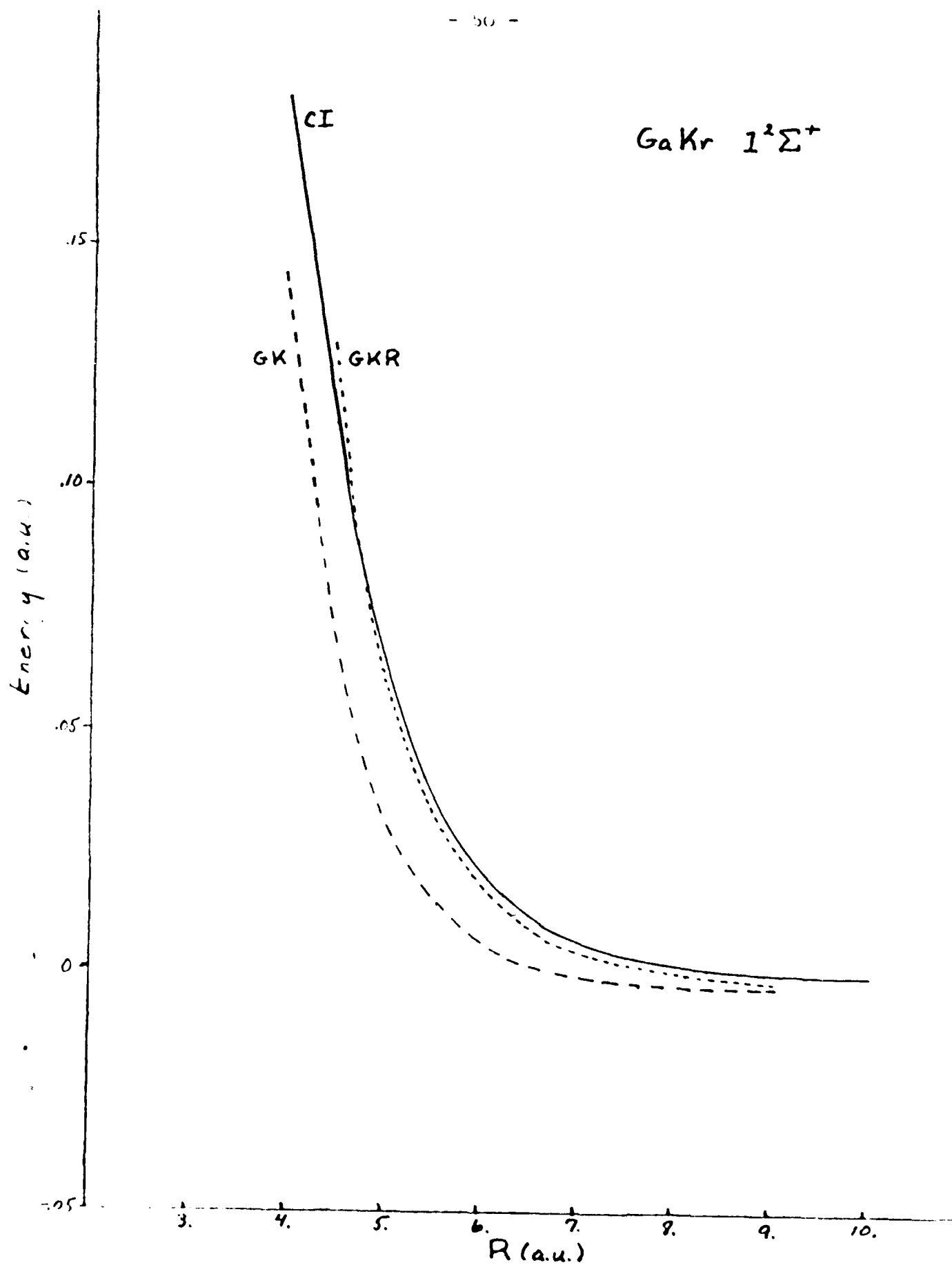
the spherically symmetric core density plus the valence density. For Ga in the ground state ($4s^2 4p^1$), the valence density is constrained to be in a p orbital directed along the internuclear axis, to form a Σ molecular state, or perpendicular to it to form a Π state.

In order to expedite the evaluation of integrals, the atomic density is expanded in a set of Slater basis functions with the coefficients determined by a least-squares fit [4]. The basis set expansions for the density are then read into the GK program which calculates the interaction energy by three-dimensional numerical quadrature.

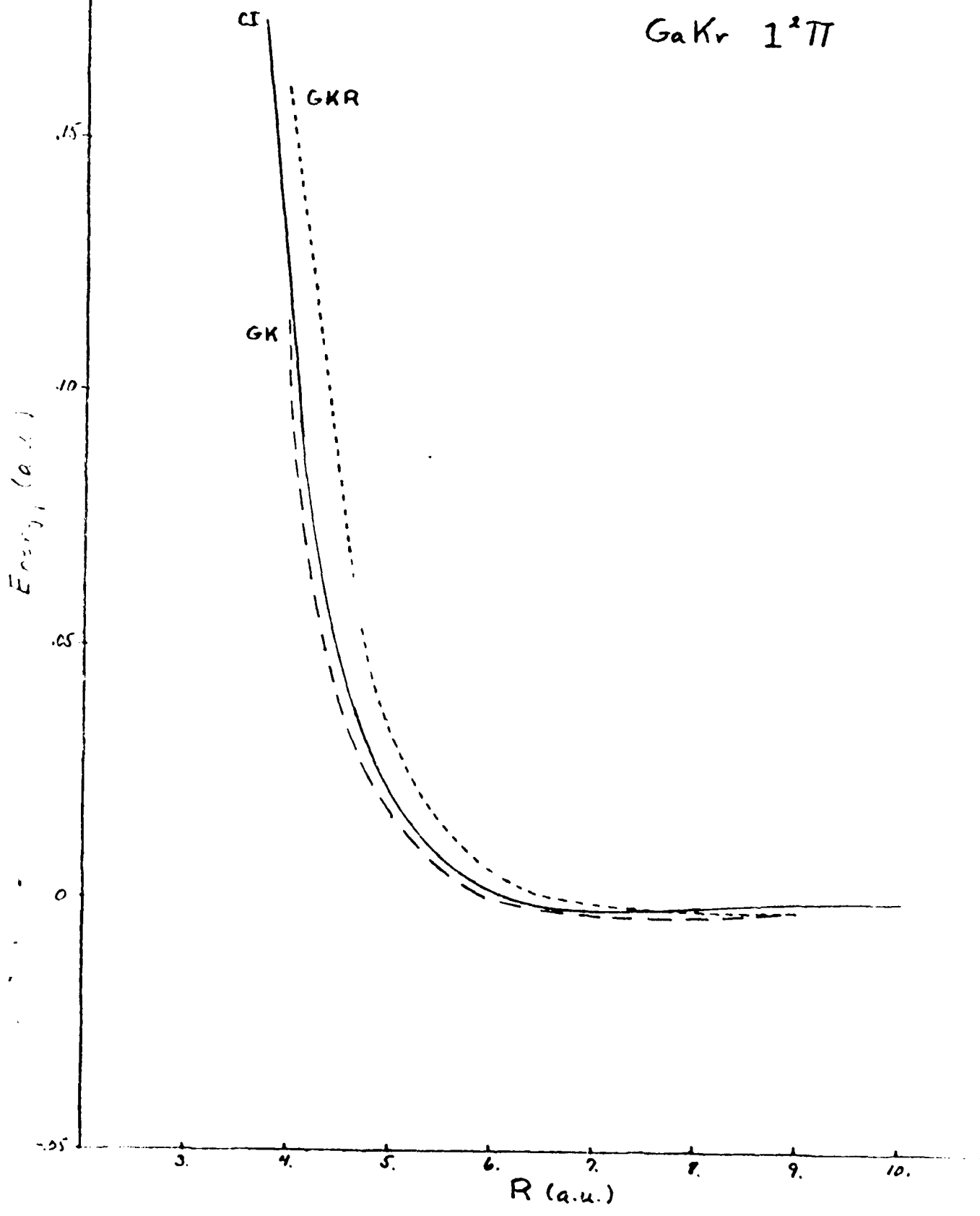
We have obtained numerically tabulated, relativistic Hartree-Fock densities for the group IIIB and rare gas atoms from Joseph Mann [10]. The densities of the $4s^2 4p^1$ and $4s^2 5s^1$ states of Ga and the ground state of Kr were fit with small sets of Slater functions. At this time the fit of the basis set expansion is not very good ($\sim 10\%$).

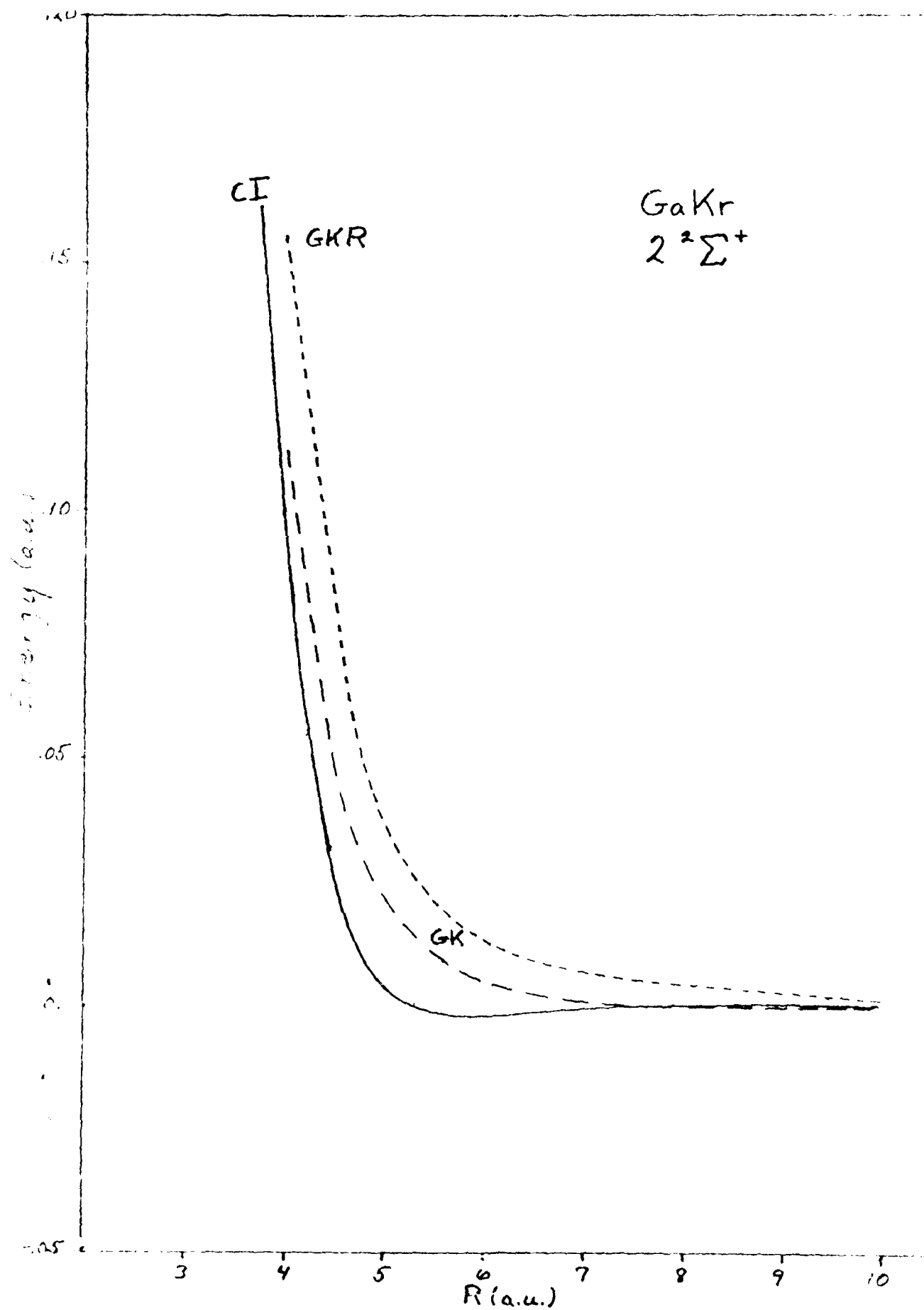
The basis set expansions obtained from this fitting procedure were then used to calculate the GK interaction energies. Because the fitting procedure does not normalize the density, the inaccuracy of the present expansions results in a spurious Coulomb repulsion between the two atoms. We hope that improving the basis set fit will correct this error.

The GK potential curves are compared with the CI results (see Section II) in Figures 1-3. The energies are plotted with respect to the asymptotic energy of each state. The curve labeled GKR includes Rae's correction while the GK curve is the unmodified GK theory. The GKR curve for the $1^2\Sigma^+$ state agrees remarkably well with the CI result. Unfortunately, the agreement for both the $1^2\Pi$ and $2^2\Sigma^+$ states are not as good. Specifically the depths and positions of the potential wells are not predicted accurately. We are currently working on improving the basis set fit and thereby the interaction energies.



GaKr $1^2\Pi$





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§4

4.1 Theoretical basis

A. Introduction

This section describes the theoretical basis of our calculations using the effective potential method. For an excimer system AB, where A is a closed-shell system, most of the states of interest correspond to the asymptotic situation where B is excited but A is in its ground state. Fundamentally, what the electron scattering theory says is that any charged particle in B sees a potential (Σ_A), due to the closed-shell system A, which is the same as if the charged particle were scattered off of A. This scattering potential is corrected for the fact that A is "depolarised" relative to the scattering problem, due to the presence of the nucleus and other electrons of B. The unique aspect of this work, which distinguishes it from many other high-quality attempts to produce such curves, is that it is based on the model interaction potentials and response functions that arise out of many body theory (using Schwinger Functional Derivatives). The use of this type of many body theory has characterized the work of this group over the last few years.¹⁶

The effective potential method will clearly give incorrect results when any of three situations are met: First, if charge transfer states mix with the excited states of interest; second, when states go asymptotically to two excited atoms; third, when covalent bonding is important. Only for charge transfer do we have a possible Class I solution. For the moment it is hoped that all three problem situations will be avoided for the lowest excimer excited states in the systems of interest to this proposal. If Zn_2 and Mg_2 are any guide the first two problems occur only for the higher excited states.¹⁷

In part B the basic equations are presented and possible methods for calculating the interaction energy are discussed in part C. The use of semiempirical forms for the effective potentials are discussed in part D.

B. The Basic Equations

Using many-body field theoretic methods it has been shown that the change in energy, ϵ , resulting from the addition of an electron to a closed-shell reference system (referred to here as A) is given by the one-particle Dyson equation

$$T(r)\phi(r) + \int dr' \Sigma^A(r;r';\epsilon)\phi(r) = \epsilon\phi(r) \quad (1)$$

where T is the kinetic energy operator and ϕ is the Dyson amplitude with r and r' being space-spin coordinates. Thus, the problem reduces to an effective one-particle problem in which this particle experiences an effective potential, Σ^A , which represents all the other particles collectively, taking into account all effects such as polarization, correlation and exchange, etc. As might be expected, the cost of this simple formulation is that Σ^A is an extremely complicated entity which is both nonlocal and energy dependent and which cannot rigorously be brought into closed form. However, it has been possible to develop

excellent closed form approximations to this potential which are based on well founded physical concepts. Most notable among these is the Random Phase Approximation (RPA) potential, ϵ_{RPA} , which has been very successfully used in calculating the ionization potentials, excitation energies, oscillator strengths, and elastic -scattering phase shifts for He [18]. ϵ_{RPA} has also been used to accurately calculate the ionization and excitation energies of Li [19]. Moreover, it has been shown that this ab initio potential encompasses other phenomenologically derived semiempirical potentials which have been used by other workers with great success [20].

It has also been recently demonstrated that by applying the same many-body techniques to the problem of two electrons added to a closed-shell reference system (A) one obtains an effective two-particle equation for the resulting change in energy [21].

$$\left[\sum_{i=1}^2 \left(T(r_i) + \int dr' \epsilon^A(r_i; r'; \epsilon) \right) + \frac{1}{|r_1 - r_2|} + \int dr_1' dr_2' W^A(r_1, r_2; r_1', r_2') \right] \phi(r_1, r_2) = \epsilon \phi(r_1, r_2), \quad (2)$$

where in addition to the individual one-particle potentials there now appears a two-particle effective potential, W^A , which represents how the presence of one particle affects the potential seen by the other particle and which reflects the fact that system A can act as a dielectric medium to shield the Coulombic interaction between two charged particles. As with ϵ^A , this potential cannot be rigorously brought into closed form.

However, an excellent ab initio closed form approximation to this potential can be obtained with the Random Phase Approximation, W_{RPA} , which is completely compatible with the similarly obtained one-particle potential, Σ_{RPA} .

If we now proceed to the case of adding m electrons to our closed-shell reference system it follows by induction and can be proven formally that the change in energy is given by

$$\begin{aligned} & \left[\sum_{i=1}^m \left(T(r_i) + \int dr'_i \Sigma^A(r_i; r'_i; \epsilon) \right) + \sum_{i>j}^m \left(\frac{1}{|r_i - r_j|} + \int dr'_i dr'_j W^A(r_i r_j; r'_i, r'_j; \epsilon) \right) \right. \\ & \left. + \sum_{j>k}^m \int dr'_i dr'_j dr'_k U^A(r_i, r_j, r_k; r'_i, r'_j, r'_k; \epsilon) + \dots + \int dr'_1 \dots dr'_m V^A(r_1 \dots r_m; r'_1 \dots r'_m; \epsilon) \right] \Psi(r_1 \dots r_m) \\ & = \epsilon \Psi(r_1 \dots r_m), \end{aligned} \quad (3)$$

where our notation for three-particle and higher potentials is obvious.

In the above we only considered the addition of electrons to our closed-shell reference system A. However, we can also add nuclei as well; the only difference being that when acting on a nuclear coordinate all potential terms involving electron exchange must of course vanish. Since this can be trivially accomplished by choosing an appropriate (artificial) nuclear spin coordinate, we can immediately generalize (3) to include both nuclei and electrons by allowing the particles to carry different charges, z , (where $z = -1$ for an electron) to give

$$\begin{aligned} & \left[\sum_{i=1}^m (T(r_i) - \int dr'_i \Sigma^A(r_i; r'_i; \epsilon, z_i)) + \sum_{i>j}^m \left(\frac{z_i z_j}{|r_i - r_j|} + \int dr'_i dr'_j W^A(r_i, r_j; r'_i, r'_j; \epsilon, z_i, z_j) \right) \right. \\ & \left. + \dots \right] \Psi(r_1 \dots r_m) = \epsilon \Psi(r_1 \dots r_m). \end{aligned} \quad (4)$$

We of course cannot solve (4) since the potentials involved cannot be written in closed form. However, we can replace these potentials by their RPA approximates which are in closed form. Furthermore, realizing that we are deriving a theory for intermolecular forces which is essentially perturbative in nature, we will now assume that all three-particle and higher potentials can be neglected so that our equation becomes simply

$$\begin{aligned} & \left[\sum_{i=1}^m (T(r_i) - \int dr'_i \Sigma^A(r_i; r'_i; \epsilon, z_i)) + \sum_{i>j}^m \left(\frac{z_i z_j}{|r_i - r_j|} + \int dr'_i dr'_j W^A(r_i, r_j; r'_i, r'_j; \epsilon, z_i, z_j) \right) \right] \Psi(r_1 \dots r_m) \\ & = \epsilon \Psi(r_1 \dots r_m). \end{aligned} \quad (5)$$

Since our interest lies in the calculation of potential energy surfaces, what we really want is an equation for the change in energy when m_e electrons and m_n nuclei are added to A with these nuclei held fixed at specific points in space (which we will refer to collectively as R with the actual spatial coordinate of nuclei i being R_i). That is, we want to be able to separate electronic motion from nuclear motion so that this quantity, $\mathcal{E}(R)$, will be the total potential experienced by these nuclei and will satisfy the equation

$$\left[\sum_{i=1}^{m_n} T(R_i) + \mathcal{E}(R) \right] X(R) = \epsilon X(R) \quad (6)$$

where $X(R)$ is a function of the nuclear coordinates only. As it stands, (5) precludes such a separation because of the energy dependence of the potentials involved. To overcome this problem we will now assume that for those solutions to (5) we seek this energy dependence is not strong. Furthermore, we will also assume that the response of A to the added particles is instantaneous. In this way we can replace the non-adiabatic energy dependent potentials in (5) with their hermitian energy independent adiabatic approximates such as those given in ref.21. With these substitutions (5) does become separable, and by taking

$$\psi(r_1 \dots r_m) = \sum_j X_j(R) \psi_j(r_1 \dots r_{m_e}) ; \langle \psi_i | \psi_j \rangle = \delta_{ij} \quad (7)$$

where $\psi(r_1 \dots r_{m_e})$ is a function of only the electronic coordinates we find that $\mathcal{E}(R)$ is given by

$$\mathcal{E}(R) = E^A(R) - \sum_{i=1}^{m_n} \epsilon^A(R_i; z_i) + \sum_{i>j}^{m_n} \left(\frac{z_i z_j}{|R_i - R_j|} + W^A(R_i, R_j; z_i, z_j) \right), \quad (8)$$

where E^A is given by the equation

$$\begin{aligned} & [H(r_1 \dots r_{m_e}; R) + \sum_{i=1}^{m_e} \left(\int dr'_i \epsilon^A(r; r'_i) - \sum_{j=1}^{m_n} \int dr'_j W^A(r_i, R_j; r'_j; z_j) \right) \\ & + \sum_{i>j}^{m_e} \int dr'_i dr'_j W^A(r_i, r_j; r'_i r'_j)] \psi(r_1 \dots r_{m_e}) = E^A(R) \psi(r_1 \dots r_{m_e}) \end{aligned} \quad (9a)$$

where H is the usual hamiltonian for m_e electrons in the field of m_n fixed nuclei

$$\begin{aligned}
 H(r_1 \dots r_{m_e}; R) &= \sum_{i=1}^{m_e} (T(r_i) - \sum_{j=1}^{m_n} \frac{z_j}{|r_i - R_j|}) + \sum_{i>j}^{m_e} \frac{1}{|r_i - r_j|} \\
 &= \sum_{i=1}^{m_e} h(r_i) + \sum_{i>j}^{m_e} \frac{1}{r_{ij}}
 \end{aligned} \tag{9b}$$

and where all one- and two-particle effective potentials are taken to be hermitian adiabatic approximates to the true potentials. Note also that all potential terms involving the m_n nuclei are now written as local quantities thereby taking into account the previously mentioned fact that there are no exchange (i.e. nonlocal) terms in the potentials when nuclei are being considered.

If we now collectively refer to these m_e electrons and m_n nuclei which have a fixed internuclear geometry as being system B, then $\mathcal{E}(R)$ is the change in energy resulting from the creation of system B in the vicinity (as measured by R) of A. If $R \rightarrow \infty$ then $\mathcal{E} \rightarrow \mathcal{E}_B^0$ which is just the energy B itself. Therefore, the intermolecular potential of the system A-B as a function of the separation between A and B is

$$V_B^A(R) = E_B^A(R) - E_B^0 + V_{B,nuc}^A(R) \tag{10a}$$

where

$$V_{B,nuc}^A(R) = - \sum_{i=1}^{m_n} \Sigma^A(R_i; z_i^B) + \sum_{i>j}^{m_n} W^A(R_i, R_j; z_i^B, z_j^B) \tag{10b}$$

and where

$$E_B^0 = \mathcal{E}_B^0 + \sum_{i>j}^{m_n} z_i^B z_j^B \frac{1}{|R_i - R_j|} \quad (10c)$$

is just the electronic energy of isolated system B and where $E_B^A(R)$ is given by

$$\begin{aligned} & [H(r_1 \dots r_{m_e}; R) + \sum_{i=1}^{m_e} \int dr'_i (\Sigma^A(r_i; r'_i) - \sum_{j=1}^{m_n} W^A(r_i, R_j; r'_i; Z_j^B)) \\ & + \sum_{i>j}^{m_e} \int dr'_i dr'_j W^A(r_i, r_j; r'_i r'_j)] \Psi_B^A(r_1 \dots r_{m_e}) = E_B^A(R) \Psi_B^A(r_1 \dots r_{m_e}) \quad (10d) \end{aligned}$$

Therefore, given that we know E_B^0 and that we have available good closed form adiabatic approximates for Σ^A and W^A our problem reduces to finding the solutions (or rather a particular solution) to (10d). In the following section we will look at some ways of doing this.

C. Determination of E_B^A

Our equation for E_B^A is of the form

$$(H + U^A) \psi_B^A = E_B^A \psi_B^A \quad (11a)$$

where

$$\begin{aligned} U^A(r_1 \dots r_{m_e}; R) &= \sum_{i=1}^{m_e} \int dr_i' [\Sigma^A(r_i; r_i') - \sum_{j=1}^{m_n} W^A(r_i, R_j; r_i'; Z_j^B)] \\ &+ \sum_{i>j}^{m_e} \int dr_i' dr_j' W^A(r_i, r_j; r_i', r_j') \\ &= \sum_{i=1}^{m_e} p^A(r_i) + \sum_{i>j}^{m_e} q_{12}^A(r_i, r_j) \end{aligned} \quad (11b)$$

where we note that ψ_B^A is an eigenfunction of the hermitian 'hamiltonian' $(H + U^A)$ and that H is the electronic hamiltonian for isolated system B . If we now explicitly assume that U^A is small compared to H (this of course was implicit in our derivation of U^A in the first place) then U^A can be regarded as being a small perturbation on H . As a consequence, the solution, ψ_B^A , to (11) which we seek should resemble the electronic wavefunction for isolated system B , ψ_B^0 , and this wavefunction should therefore provide us with a proper starting point determining ψ_B^A and E_B^A .

1. First-Order Perturbation Treatment

Projecting (11a) against ψ_B^A and normalizing ψ_B^A to unity gives

$$E_B^A = \langle \psi_B^A | H + U^A | \psi_B^A \rangle ; \langle \psi_B^A | \psi_B^A \rangle = 1 , \quad (12a)$$

whereas if ψ_B^0 is a self-consistent solution for isolated system B its energy is.

$$E_B^0 = \langle \psi_B^0 | H | \psi_B^0 \rangle ; \langle \psi_B^0 | \psi_B^0 \rangle = 1 . \quad (12b)$$

If we assume that U^A is a quite small perturbation to H then we can solve for E_B^A using standard first-order perturbation theory to obtain

$$E_B^A = E_B^0 + \langle \psi_B^0 | U^A | \psi_B^0 \rangle \quad (13)$$

so that our first-order perturbative expression for V_B^A is simply

$$V_B^A = V_{B,nuc}^A + \langle \psi_B^0 | U^A | \psi_B^0 \rangle . \quad (14)$$

This of course is equivalent to assuming that the wavefunction for system B remains virtually unchanged when in the presence of A .

In terms of the one- and two-particle density matrices, ρ_1^0 and ρ_2^0 , associated with ψ_B^0 , (14) becomes

$$V_B^A = V_{B,nuc}^A + \int_{r'=r} dr p^A(r') \rho_1^0(r;r') + \int_{r'=r} dr_1 dr_2 q_{12}^A(r_1, r_2) \rho_2^0(r_1, r_2; r_1' r_2'). \quad (15)$$

If ψ_B^0 is a single Slater determinant so that

$$\rho_2^0(r_1, r_2; r_1', r_2') = 1/2 [\rho_1^0(r_1; r_1') \rho_1^0(r_2; r_2') - \rho_1^0(r_1; r_2') \rho_1^0(r_2; r_1')] \quad (16a)$$

with

$$\rho_1^0(r; r') = \sum_{i=1}^n \phi_i^*(r) \phi_i(r') \quad (16b)$$

where $\{\phi_i\}$ are the n one-electron spin-orbitals comprising ψ_B^0 ,
then V_B^A takes on the form

$$V_B^A = V_{B,nuc}^A + \sum_{i=1}^n \langle \phi_i | p^A | \phi_i \rangle + 1/2 \sum_{i \neq j}^n [\langle \phi_i \phi_j | q_{12}^A | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | q_{12}^A | \phi_j \phi_i \rangle] \quad (17)$$

where the two-electron integrals over q_{12}^A are written in the standard
 $\langle 12 || 12 \rangle$ notation.

If ψ_B^0 cannot be written as a single Slater determinant but can
be written as a linear combination of determinants involving n one-electron
spatial orbitals $\{\phi_i^0\}$ then (12b) can always be written as

$$E_B^0 = \sum_{i,j}^n D_{ij}^j \langle \phi_i^0 | h | \phi_j^0 \rangle + \sum_{i,j,k,l}^n D_{ij,kl}^{kl} \langle \phi_i^0 \phi_j^0 | \frac{1}{r_{12}} | \phi_k^0 \phi_l^0 \rangle \quad (18)$$

where $\{D_{ij}^j, D_{ij,kl}^{kl}\}$ are fixed coefficients which depend on the precise form
of ψ_B^0 and on orbital overlaps. Since U^A is of the same form as H
and, like H , is spin independent (recall that isolated system A must
be closed-shell) we can immediately write our first-order approximation
for V_B^A as

$$V_B^A = V_{B,nuc}^A + \sum_{i,j}^n D_{ij}^j \langle \phi_i^0 | p^A | \phi_j^0 \rangle + \sum_{i,j,k,l}^n D_{ij}^{kl} \langle \phi_i^0 \phi_j^0 | q_{12}^A | \phi_k^0 \phi_l^0 \rangle \quad (19)$$

where all operators and integrals are now explicitly taken to involve only spatial coordinates. Therefore, we can determine $\langle \psi_B^0 | U^A | \psi_B^0 \rangle$ by using the general energy expression (18) but employing one- and two-electron integrals over the operators p^A and q_{12}^A instead of the usual integrals over \hbar and $\frac{1}{r_{12}}$.

We could continue this perturbation treatment by going on to determine second-order and higher corrections. However we will stop here and next consider a self-consistent approach instead.

2. Self-Consistent Treatment

Let us now assume that while U^A is a small perturbation to H it is not small enough to justify a simple first-order perturbation treatment. That is, we will now assume that ψ_B^A can still be taken to be functionally the same as ψ_B^0 but because of the presence of A the spatial orbitals themselves distort away from $\{\phi_i^0\}$ to a meaningful extent. The problem is then to determine these new orbitals $\{\phi_i\}$. Since ψ_B^A is an eigenfunction of electronic motion satisfying (11) this can be done variationally. That is, we can determine these new distorted orbitals by requiring that E_B^A be stationary with respect to changes in these orbitals. If for simplicity (but not necessity) we assume that ψ_B^0 can be written as a Hartree-Fock type wavefunction involving orthonormal

spatial orbitals (or orthonormal spin-orbitals for the case of an Unrestricted Hartree-Fock wavefunction) then (18) takes on the simple Roothaan form

$$E_B^0 = 2 \sum_{i=1}^n f_i \langle \phi_i^0 | h | \phi_i^0 \rangle + \sum_{i,j}^n [a_{ij} J_{\phi_i^0 \phi_j^0} + b_{ij} K_{\phi_i^0 \phi_j^0}] \quad (20a)$$

where

$$J_{\phi_i^0 \phi_j^0} = \langle \phi_i^0 | J_{\phi_j^0} | \phi_i^0 \rangle = \langle \phi_j^0 | J_{\phi_i^0} | \phi_j^0 \rangle = \langle \phi_i^0 \phi_j^0 | \frac{1}{r_{12}} | \phi_i^0 \phi_j^0 \rangle \quad (20b)$$

$$K_{\phi_i^0 \phi_j^0} = \langle \phi_i^0 | K_{\phi_j^0} | \phi_i^0 \rangle = \langle \phi_j^0 | K_{\phi_i^0} | \phi_j^0 \rangle = \langle \phi_i^0 \phi_j^0 | \frac{1}{r_{12}} | \phi_j^0 \phi_i^0 \rangle \quad (20c)$$

and where $\{f_i; a_{ij}; b_{ij}\}$ are fixed coefficients (for the case of a multi-configurational wavefunction these coefficients are simply related to the variationally determined configurational coefficients) which depend on the precise form of ψ_B^0 . Since ψ_B^A is being taken to have the same form as ψ_B^0 and because of the similarities between H and U^A mentioned above, we can immediately write our equation for E_B^A as

$$E_B^A = 2 \sum_{i=1}^n f_i \langle \phi_i | h^A | \phi_i \rangle + \sum_{i,j} [a_{ij} \langle \phi_i \phi_j | g_{12}^A | \phi_i \phi_j \rangle + b_{ij} \langle \phi_i \phi_j | g_{12}^A | \phi_j \phi_i \rangle] \quad (21a)$$

where the operator h^A and g_{12}^A are given by

$$h^A = h + p^A ; g_{12}^A = \frac{1}{r_{12}} + q_{12}^A \quad (21b)$$

Therefore, $\{\phi_i\}$ and therefore E_B^A can be determined using standard basis set expansion (LCAO) SCF techniques. The only difference is that instead of using the usual one- and two-electron integrals we must use integrals over the operators h^A and g_{12}^A instead. However, since these integrals serve only as input this difference is transparent to whatever available SCF procedure we employ.

3. Configuration Interaction Treatment

For the sake of completeness it should be mentioned that since ψ_B^A can be variationally determined there is no need to stop at the SCF level and we could solve for this function as a Configuration Interaction (CI) problem. The only difference from a standard CI calculation is that instead of using the usual one- and two-electron integrals we must use integrals over the h^A and g_{12}^A operators defined in (21b). It should be pointed out however that any solution for ψ_B^A which differs significantly from ψ_B^0 implies that for that solution U^A can no longer be regarded as a small perturbation to H and in such a case the validity of the approximations made in our choice of U^A would become subject to question. This of course also applies in our SCF treatment as well.

D. The Potentials

The one- and two-particle effective potentials Σ^A and W^A appearing in our final equations in section II are hermitian adiabatic approximates to the true field theoretic potentials. As we have mentioned,

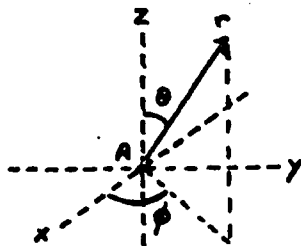
such potentials can be obtained in closed ab initio form using many-body theory within the framework of the RPA approximation and taking the adiabatic limits. However, while these potentials are tractable they are nonetheless quite complicated and their use would entail considerable computational effort. In view of the perturbative nature of our theory it is reasonable to expect that we could use potentials having simpler forms. Such simpler potentials can be obtained by making moment expansions of the RPA potentials and truncating these expansions in a physically meaningful manner [21]. When this is done, the resulting potentials can be cast in forms which are very similar to phenomenologically derived semiempirical potentials which have been used by other workers with considerable success [22]. Therefore, it would seem that the use of complicated ab initio potentials is not warranted (although we do reserve the option to do so) and that we can take our potentials to have semiempirical forms similar to those used by Dalgarno and by Victor [22], namely

$$\begin{aligned} \int dr' \Sigma^A(r;r') = & -\frac{Z^A}{|r|} + \int dr' \Sigma_{HF}^A(r;r') - \frac{\alpha_d^A}{2|r|^4} W_6(k|r|) \\ & - \frac{\alpha_q^A}{2|r|^6} W_8(k|r|) + (a_0 + a_1|r| + a_2|r|^2)e^{-k|r|} \end{aligned} \quad (22a)$$

and

$$\begin{aligned} \int dr'_1 dr'_2 W^A(r_1, r_2; r'_1, r'_2) = & -\frac{\alpha_d^A}{|r_1|^2 |r_2|^2} W_3(k|r_1|) W_3(k|r_2|) P_1(\cos \gamma_{12}) \\ & - \frac{\alpha_q^A}{|r_1|^3 |r_2|^3} W_4(k|r_1|) W_4(k|r_2|) P_2(\cos \gamma_{12}) \end{aligned} \quad (22b)$$

where we have chosen our coordinate system to be centered on A which for simplicity we now take to be an atom having a nuclear charge of z^A



and where

$W_n(x) = (1 - e^{-x^n})$ is a cutoff function

γ_{12} = angle between vectors r_1 and r_2

$P_\ell(x)$ = legendre polynomial of the ℓ^{th} degree

α_d^A = dipole polarizability of A

α_q^A = approximate quadrupole polarizability of A (adjustable)

k = approximately $1/2 r_0$ where r_0 is the effective radius of A (adjustable)

$\{a_i\}$ = adjustable monopole parameters

and

$$\Sigma_{\text{HF}}^A(r; r') = \sum_{i=1}^{n_A} \frac{\phi_i^{A*}(r') [2 - P_{r, r'}] \phi_i^A(r')}{|r - r'|}$$

is the static Hartree-Fock potential of A with $\{\phi_i^A\}$ being the n_A spatial Hartree-Fock orbitals for the electrons in A. $P_{r, r'}$ is the permutation operator if r is an electronic coordinate whereas $P_{r, r'} = 0$

if r is a nuclear coordinate. Note that all quantities are now purely spatial and that Σ^A and W^A are therefore explicitly spin independent.

In (22a) the first term is simply the potential due to the nucleus of A and the second term is the static Hartree-Fock potential for the electrons in A occupying the spatial orbitals $\{\phi_i^A\}$. The next two terms in (22a) are asymptotically correct induced dipole and quadrupole polarization potentials which die off rapidly at short distances from A . The final term is an induced monopole term which serves as a short range correction potential. The terms in (22b) describe an asymptotically correct dielectric potential which properly cancels out one-particle induced dipole and quadrupole polarizations of A due to two particles of the same charge when these particles are on opposite sides of A . That these potentials represent a significant simplification over the ab initio potentials is clear in that our two-particle potential is strictly local and the only nonlocal term in the one-particle potential is simply the usual Hartree-Fock exchange potential. However, despite their simplicity, potentials such as these have been used very successfully for a variety of problems in the past and should therefore be quite adequate for our purposes.

As it stands, (22b) is concise and to the point. However, one important property is obscured. This is that our two-particle potential can be written in terms of one-particle operators only. To see this we need only express the angle γ_{12} in terms of the spherical angles

for each vector. Thus, by making use of the expansion

$$P_\ell(\cos \gamma_{12}) = P_\ell(\cos \theta_1)P_\ell(\cos \theta_2) + 2 \sum_{m=1}^{\ell} \frac{(\ell-m)!}{(\ell+m)!} P_\ell^m(\cos \theta_1)P_\ell^m(\cos \theta_2) [\cos m\phi_1 \cos m\phi_2 + \sin m\phi_1 \sin m\phi_2] \quad (24)$$

where $P_\ell^m(x)$ is an associated Legendre polynomial, we find that (22b) can be rewritten as

$$\int dr_1' dr_2' W^A(r_1, r_2; r_1', r_2') = - \sum_{i=1}^8 Q_i(r_1)Q_i(r_2) \quad (25a)$$

where

$$\begin{aligned} Q_1(r) &= \sqrt{\alpha_d^A} |r|^{-2} W_3(k|r|) P_1(\cos \theta) \\ Q_2(r) &= \sqrt{\alpha_d^A} |r|^{-2} W_3(k|r|) P_1^1(\cos \theta) \cos \phi \\ Q_3(r) &= \sqrt{\alpha_d^A} |r|^{-2} W_3(k|r|) P_1^1(\cos \theta) \sin \phi \\ Q_4(r) &= \sqrt{\alpha_q^A} |r|^{-3} W_4(k|r|) P_2(\cos \theta) \\ Q_5(r) &= 1/3 \sqrt{\alpha_q^A} |r|^{-3} W_4(k|r|) P_2^1(\cos \theta) \cos \phi \\ Q_6(r) &= 1/3 \sqrt{\alpha_q^A} |r|^{-3} W_4(k|r|) P_2^1(\cos \theta) \sin \phi \\ Q_7(r) &= 1/12 \sqrt{\alpha_q^A} |r|^{-3} W_4(k|r|) P_2^2(\cos \theta) \cos 2\phi \\ Q_8(r) &= 1/12 \sqrt{\alpha_q^A} |r|^{-3} W_4(k|r|) P_2^2(\cos \theta) \sin 2\phi \end{aligned} \quad (25b)$$

Consequently, the implementation of this method involves the addition of only one-electron integrals to existing SCF or CI programs. In addition, if $\Sigma_{\text{HF}}^{\text{A}}$ is replaced by a pseudopotential, only the atomic orbitals of B will be used to calculate the potential for AB.

4.II Details of the Calculation

In developing a program package to implement the effective potential method, our goal was to make the package as general as possible. To achieve this, we have made our effective potential program EFFPOT compatible with the GVB II¹⁰ SCF and CI programs. This program package is a gaussian basis function, molecular SCF and CI routine which will enable the present version of EFFPOT to be extended to large molecules. The version of GVB II that we are using has an option for replacing the atomic cores by a pseudopotential; however, the form of this built-in pseudopotential is different from those being developed for large atoms¹¹. The modifications needed to make use of available pseudopotentials would be relatively easy.

The GVB II program package consists of a number of sequential program steps which are outlined below.

- | | |
|---------------------------|--|
| 1. Integral generation | a) PLYLABS - creates list of unique
integral labels |
| | b) PLYINTS - evaluates integrals |
| 2. Integral preprocessing | a) PLYIJLK } convert output of PLYINTS |
| | b) PLYPAIR } to form needed for input
to GVB II |
| 3. SCF | GVB II |
| 4. CI | a) CORTRN transforms to molecular basis |
| | b) CIPROG |

To perform an effective potential calculation, the program EFFPOT is inserted between steps 2a and 2b.

EFFPOT calculates the additional integrals required, $\langle \phi_i | \Sigma^A | \phi_j \rangle$ and $\langle \phi_i | Q_n | \phi_j \rangle$, and modifies the integral tape so that the insertion of an effective potential is transparent to GVB II. These integrals have not been previously evaluated for gaussian basis sets, and because of the cut-off functions in Σ^A and Q_n and the angular dependence of Q_n , the evaluation of these integrals is rather complicated, especially for two-center integrals containing basis functions for $l > 0$.

Although it is relatively easy to construct an algorithm for evaluating these integrals, the algebraic detail rapidly becomes overwhelming. To alleviate this problem, we used the algebraic programming system REDUCE³ to produce the FORTRAN code required to evaluate these integrals. An explanation of the algorithm used to derive the integral expressions and an example of the input to REDUCE are given below for one of the more complicated integrals.

The integral we shall consider is

$$\langle P_x^E | Q_4^B | P_x^F \rangle \quad (13)$$

where the superscripts indicate the atomic center on which the (basis or potential) function is centered, Q_4 is defined by equation 10b and P_x indicates a "p_x" gaussian basis function. This integral can be written explicitly as

$$\begin{aligned} \langle P_x^E | Q_4^B | P_x^F \rangle &= \\ &= \sqrt{d_q^A/3} \int d\tau x_E e^{-\alpha r_E^2} r_0^{-3} W_4(kr_0) P_2(\cos \theta_0) x_F e^{-\beta r_F^2} \\ &= \sqrt{d_q^A/3} I. \end{aligned} \quad (14)$$

Using the relation

$$P_2(\cos \theta_0) = \frac{3z_0^2 - r_0^2}{2r_0^2}, \quad (15)$$

we can write

$$\begin{aligned} I &= \frac{3}{2} \int d\tau x_E e^{-\alpha r_E^2} W_4(kr_0) z_0^2 r_0^{-5} x_F e^{-\beta r_F^2} \\ &\quad - \frac{1}{2} \int d\tau x_E e^{-\alpha r_E^2} W_4(kr_0) r_0^{-3} x_F e^{-\beta r_F^2} \\ &\equiv I_1 + I_2. \end{aligned} \quad (16)$$

In order to obtain the term $z_B^2 e^{-cr_B^2}$, we will set up a fake gaussian on center B, $e^{-cr_B^2}$, and move the $W_4(kr_B)/r_B^5$ term to a fake center, D; after evaluating the resulting integral, we will take the limits $D \rightarrow B$ and $c \rightarrow 0$. Using the relation

$$z_B^2 e^{-cr_B^2} = \frac{1}{2^2 c^2} \frac{\partial^2}{\partial B_z^2} e^{-cr_0^2} + \frac{1}{2c} e^{-cr_0^2}, \quad (17)$$

we obtain

$$I_1 = \lim_{c \rightarrow 0} \lim_{D \rightarrow B} \frac{3}{2} \frac{1}{2^2 \alpha \beta} \frac{\partial^2}{\partial E_x \partial F_x} \left\{ \frac{1}{2^2 c^2} \frac{\partial^2}{\partial B_z^2} I_3 + \frac{1}{2c} I_3 \right\} \quad (18)$$

where

$$I_3 = \int d\tau e^{-\alpha r_E^2} e^{-cr_0^2} r_0^{-5} W_4(kr_0) e^{-\beta r_F^2}. \quad (19)$$

We can also write

$$I_2 = \frac{-1}{2^3 \alpha \beta} \frac{\partial^2}{\partial E_x \partial F_x} I_4 \quad (20)$$

where

$$I_4 = \int d\tau e^{-\alpha r_E^2} e^{-\beta r_F^2} r_0^{-3} W_4(kr_0). \quad (21)$$

We can then apply the rule for combining gaussians on two centers,

$$e^{-\alpha r_E^2} e^{-\beta r_F^2} = e^{-\frac{\alpha\beta}{\gamma} R_{EF}^2} e^{-\gamma r_A^2} \quad (22)$$

where $\gamma = \alpha + \beta,$ (22a)

R_{EF} is the distance between centers E and F, and center A is defined by

$$A_x = (\alpha E_x + \beta F_x) / \gamma. \quad (22b)$$

We then use the Fourier Convolution Theorem to obtain the following expressions

for I_3 and I_4 :

$$I_3 = e^{-\frac{\alpha\beta}{\gamma} R_{EF}^2} e^{-\frac{\gamma\delta}{\delta} R_{AD}^2} I_5 \quad (23)$$

where

$$I_5 = \int d\tau e^{-\delta r_G^2} r_0^{-5} W_4(kr_0) \quad (24)$$

$$= \frac{\pi}{\delta R_{0G}} \int_0^\infty dr r^{-4} W_4(kr) \left\{ e^{-\delta(r-R_{0G})^2} - e^{-\delta(r+R_{0G})^2} \right\},$$

and

$$I_4 = e^{-\frac{\alpha\beta}{\gamma} R_{EF}^2} I_6 \quad (25)$$

where

$$I_6 = \int d\tau e^{-\gamma r_A^2} r_0^{-3} W_4(kr_0) \quad (26)$$

$$= \frac{\pi}{\delta R_{A0}} \int_0^\infty dr r^{-2} W_4(kr) \left\{ e^{-\gamma(r-R_{A0})^2} - e^{-\gamma(r+R_{A0})^2} \right\}.$$

If these equations $\delta = \gamma + c$ and G is the center obtained by combining Gaussians on A and D . The derivatives and limits in equation 18 are obtained analytically by REDUCE and the result is that equation 18 is written as a sum of integrals with forms similar to those given by equations 24 and 26. These basic integrals are evaluated numerically and summed to give the result for $\langle P_x^E | Q_4^B | P_x^F \rangle$. To obtain expressions for this integral in the case where any of centers E, F, B coincide, REDUCE is used to obtain the appropriate limit ($E \rightarrow F$, for example). The REDUCE commands used to evaluate all Q_4 integrals are given in Appendix B. The output from this REDUCE code is rearranged, using additional REDUCE commands, to produce FORTRAN code which can be inserted directly in the integral evaluation subroutines.

The present versions of the EFFPOT integral routines are restricted to two centers and s or p basis functions. Our tests of this program on LiHe are described in the next section.

The integration itself is done by a 32 point Gauß integration with the IBM library program DQG 32. The other FORTRAN-programs of the EFFPOT routine, developed by ourselves, are contained in Appendix C.

4.III Test Calculations of EFFPOT on LiHe

In this section we present the results of the first stage of our tests of the effective potential method. We have chosen LiHe as the test system, and in this stage of the tests we assume that the parameters of our semi-empirical potential are known.

Values of α_d and α_q can easily be obtained; however, it should be pointed out that in a semi-empirical potential, each parameter plays a dual role. Besides describing the physical effect to which it most obviously corresponds, each parameter also serves to correct for the deficiencies of the semi-empirical model. Consequently in the best fit for the potential parameters, the values of α_d , α_q , etc., should not be expected to equal the physical quantities. The values for the cut-off functions and for the short-range part of the potential are harder to obtain. Our initial desire was to use the parameters obtained by Peach.¹² She calculated the parameters for a model potential describing one electron outside of He by fitting the parameters to electron-He atom scattering data. Her model also included a pseudopotential to represent the Hartree-Fock potential of He; this fact makes it impossible to separate the pseudopotential from the short-range terms needed for the effective potential (see equation 7). Consequently, for our test calculations, we use Peach's values for α_d , α_q , β and her cut-off functions. In addition, we have guessed a value for a_0 (equation 7), so that the short-range potential has only one term.

The exact forms of the potentials used in our test calculations are

$$\int dr' \Sigma^A(r; r'; z) = \frac{Z^A z}{r} + z \int dr' \Sigma_{HF}^A(r; r') + z^2 a_0 e^{-\gamma r} - \frac{\alpha_d z^2}{2 r^4} \omega_2(\beta r) - \frac{\alpha'_d z^2}{2 r^6} \omega_3(\beta' r) \quad (27)$$

$$\int dr'_1 dr'_2 W^A(r_1, r_2; r'_1, r'_2; z_1, z_2) = \frac{-\alpha_d z_1 z_2}{2 r_1^2 r_2^2} X_2(\beta r_1) X_2(\beta r_2) P_1(\cos \gamma_{12}) - \frac{-\alpha'_d z_1 z_2}{2 r_1^3 r_2^3} X_3(\beta r_1) X_3(\beta r_2) P_2(\cos \gamma_{12}) \quad (28)$$

Where W_n is defined by

$$W_n(x) = [X_n(x)]^2 \quad (29a)$$

and

$$X_n(x) = 1 - \exp(-x) \sum_{m=0}^n \frac{x^m}{m!} \underset{x \rightarrow 0}{\approx} \frac{x^{n+1}}{(n+1)!} \quad (29b)$$

$$\alpha' = (\alpha'_d - 6\beta_1/M).$$

The values of the parameters used are given in table 1.

In tables 2 and 3 and figures 1 and 2, we compare the effective potential-SCF (EP-SCF) calculations with SCF¹³ and restricted CI calculations for the same basis set. The basis set is that of Krauss, Maldonado and Wahl¹³.

The restricted CI calculations presented here have the same asymptotic limit as the EP-CI calculations, but do not fully allow for distortion of He at intermediate distances. In comparing these results, it should be noted that the EP-SCF results have the same $R \rightarrow \infty$ limit as the SCF calculation, but that at intermediate distances, the EP-SCF results go as $1/R^6$ while the SCF calculations cannot give this dependence. Also, the full CI calculations, which allow for more He polarization, should give more attractive interaction

Table 1. Parameters for the potential defined by equations 27 to 29, for He^a

Z_a	2.
a_0	.05
γ	1.59
α_d	1.3834
β	2.09928
α'	-2.1222
β'	0.551429
α'_q	2.11380

^aAll the parameters except a_0 and γ are taken from Peach.¹²

Table 2. LiHe total energies (in Hartrees)

N(a.u.)	EP-SCF		SCF ^a		CI (restricted)	
	2 Σ	2 Π	2 Σ	2 Π	2 Σ	2 Π
2.	-10.19137	-10.14751	-10.18797	-10.14029	-10.20229	-10.15458
3.	-10.27436	-10.22475	-10.27465	-10.22372	-10.29037	-10.23938
4.	-10.28454	-10.22723	-10.28397	-10.22646	-10.29993	-10.24232
5.	-10.28933	-10.22603	-10.28840	-10.22546	-10.30449	-10.24138
6.	-10.29166	-10.22533	-10.29113	-10.22500	-10.30722	-10.24090
8.	-10.29321	-10.22486	-10.29304	-10.22477	-10.30911	-10.24067
10.	-10.29339	-10.22476	-10.29335	-10.22473	-10.30944	-10.24065

^aKrauss, Maldonado, and Wahl¹³

Table 3. LiHe interaction energies (in Hartrees)

i(a.u.)	EP-SCF		SCF ^a		CI(restricted)		Full CI	
	2 Σ	2 Π	2 Σ	2 Π	2 Σ	2 Π	2 Σ	2 Π
2.	.10201	.07735	.10541	.08457	.10723	.09608		
3.	.01902	-.00004	.01873	.00099	.01915	.00128	.02000	
4.	.00884	-.00252	.00941	-.00175	.00959	-.00166		
5.	.00405	-.00132	.00498	-.00075	.00503	-.00072		
6.	.00172	-.00062	.00225	-.00029	.00230	-.00024		
8.	.00017	-.00015	.00034	-.00006	.00041	-.00001		
10.	-.00001	-.00005	.00004	-.00002	.00008	.00001		

^aKrauss, Maldonado, and Wahl¹³

Figure Captions

1. Interaction energy for LiHe $^2\Sigma$ state.

⊙ connected by solid line; EP-SCF results.

▣ SCF results of Krauss, Maldonado, and Wahl¹³.

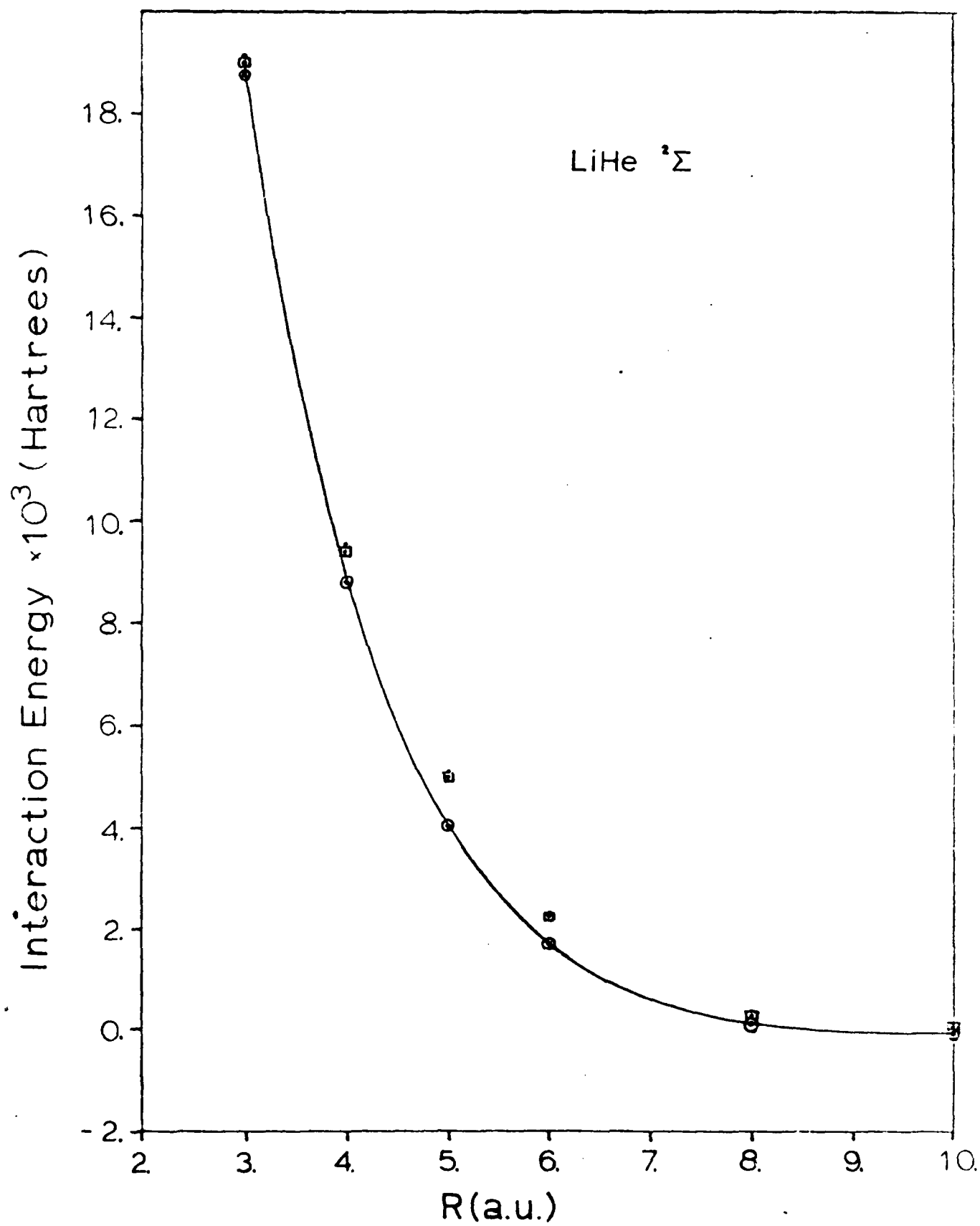
• restricted CI calculation.

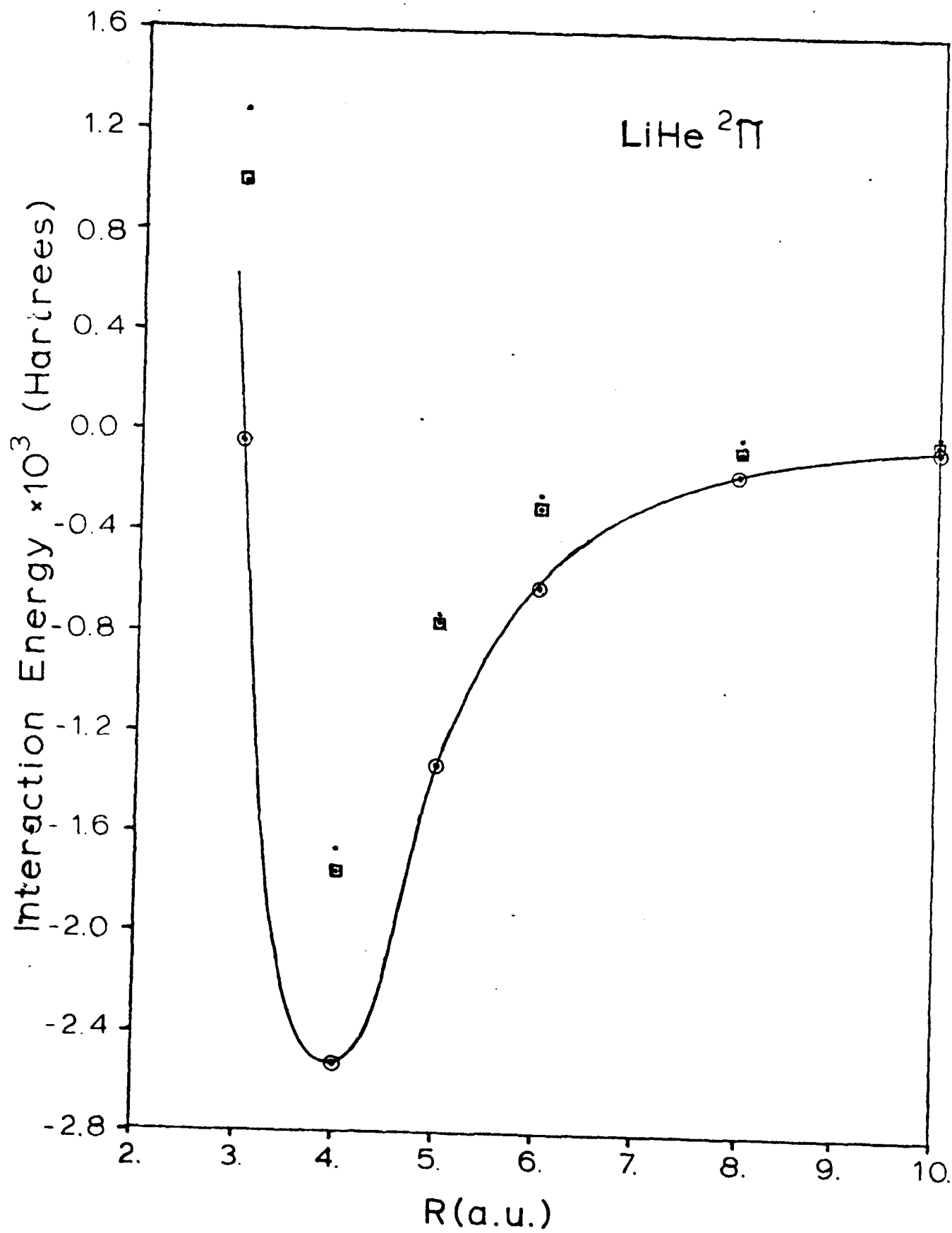
2. Interaction energy for LiHe $^2\Pi$ state.

⊙ connected by solid line; EP-SCF results.

▣ SCF results of Krauss, Maldonado, and Wahl¹³.

• restricted CI calculation.





4.IVa Test calculations of the fit program

In fig. 2 in the last paragraph it has become obvious that the initial values for the parameters in the effective potential (the ones given in table 1 in section III, let us call this set of parameters p_0 in the following) do not give a sufficiently good agreement between the calculated molecular potential curve and the curve of our CI calculation or the results of Krauss et al. One method to find a better fit would be to repeat the calculations for a large number of parameter values and so to calculate a potential curve for each point on a dense grid in the 10-dimensional parameter space. This would be the safest method to come close to the best possible fit but it would consume an enormous amount of computer time and therefore it would be contrary to our initial goal. A faster alternative is, to apply a fit program which uses as input the results of section III and tries to improve the molecular potential curve by some kind of first order perturbation calculation.

In order to explain what kind of fitting method has been used here let us for this section introduce the following notation. p is a set of 10 parameters which go into the effective potential, $W(p,R)$ is the complete effective potential for the set p of parameters and for the nuclear distance R , $\Psi(p,R)$ is the exact electronic SCF wavefunction for the nuclear distance R and for the effective potential $W(p,R)$ calculated according to the method given in section III. $V(p,R)$ is the molecular potential calculated according to the method given in section III with the effective potential $W(p,R)$ and at a nuclear distance R .

The idea of our first order perturbation approach is to calculate first the difference between the effective potentials for two sets

of parameters p_0 and p , then calculate the expectation value of this difference potential with the exact wavefunction belonging to parameter set p , and interpret this expectation value as difference in the molecular potential. In formula

$$V(p, R) = V(p_0, R) + \langle \psi(p_0, R) | W(p, R) - W(p_0, R) | \psi(p_0, R) \rangle \quad (30)$$

as justification for the application of a first order perturbation method we have first to show that the results of the exact calculation are highly linear at variation of a parameter in the effective potential. In fig. 3 the electronic energy has been calculated with the method given in section III for various values of the dipole parameter α_d and always the same values for the other parameters at the same nuclear distance of $R = 3.5$. It can be seen that the dependence of the energy on the parameter α_d is highly linear. Similar results hold for the other parameters. These calculations have also shown that the wavefunction does not change significantly under a change of a parameter. Therefore it seems that a first order perturbation approach to the fitting problem is justified. One of the inputs in any fitting program must be a value to which we want to come close. In the case here, the assumed true molecular potential curve for the He-Li 2π state is the one given by Krauss et al. We denote it in the following by $V_K(R)$. In addition, it is necessary to define the quantity, a measure of the error, which should be minimized.

We have chosen as measure of the error of the molecular potential curve $V(p, R)$ the following quantity

$$D(p) = \sum_i [V_K(R_i) - V(p, R_i)]^2 / V_K^2(R_i). \quad (31)$$

The sum i goes over all those nuclear distances at which we try to improve the function $V(p,R)$ at the moment.

This fitting for the relative error is a disadvantage in so far, that those nuclear distances R_i at which $V_K(R_i)$ is small have a higher weight than those distances at which $V_K(R_i)$ is big. Therefore the computer tries to fit $V(p,R_i)$ with the higher priority near zeros of $V_K(R_i)$.

The fitting program and all subroutines which belong to it and all those programs which are necessary in addition to the previous programs are shown in Appendix D.

Our experience running this fitting program can be summarized as follows: The fitting program is started with a particular set p_i of 10 parameters and in its 0th step it calculates the quantity $V(p_i,R)$ according to (30). For this initial step it takes about 6 minutes times the number of points, on which the curve is fitted, to calculate the integrals. Such a long time is necessary because up to now there are no optimised standard programs of quantum chemistry available for these types of integrals. It takes a long time to transform the expressions of the functions to be integrated into such a form that a library integration program can be applied. (The 32 point Gaussian integration program DQG32 by IBM ultimately has been used. If in a next step one of the parameters $\alpha_d, \alpha_q, \beta, a_0, a_1, a_2, a_3$ is changed then it is not necessary to evaluate the integrals again because these 7 parameters do not change the shape of $W(p,R)$. They go linearly into $W(p,R)$ and also the corresponding integrals are linear in these parameters. Therefore it takes only a few seconds to calculate a new $V(p_j,R)$ when p_j differs from p_i only in a parameter which goes into $W(p,R)$ linearly. The situation

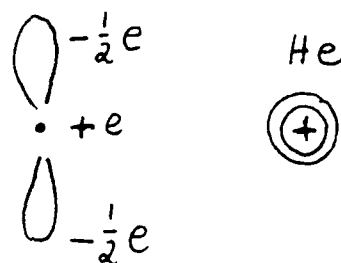
is completely different if one of the cut-off parameters is changed. Then the shape of the function $W(p,R)$ is different and it is necessary to calculate from the start the corresponding integrals again. This takes at least several minutes time. Hence it is quite time consuming to fit cut-off parameters by this fitting program. Therefore we have done the fit of cut-off parameters partly by hand.

In Fig. 4 the results of the fit can be seen for two sets of parameters which gave the best fits we could obtain for the molecular potential curve of the $^2\pi$ state of HeLi. For comparison we show in addition the curve calculated by Krauss et al. as solid line. This curve agrees quite well with our CI calculations (see Fig. 2 in section III). The result of the SCF calculations from section III is shown as dotted line also for comparison. This line is the molecular potential curve which belongs to the parameter set p_0 and it is the 0th order result of the fitting procedure in this section. The broken line and the chain line show the 1st order results for two different sets of parameters. It is obvious that the deviation between these first order curves and the Krauss et al. curve is a lot less than the deviation between the 0th order curve and the Krauss et al. curve. The worst error of our 1st order curves is in the region near $R=5$ to $R=6$. In this region it has not been possible to get a curve which is steep enough. All considered 1st order curves with a reasonable over all shape have been too horizontal in this interval. Up to now we did not yet have time to make calculations for molecular potential curves of other states of LiHe than the $^2\pi$ state. Before we do this, it would be useful to try out a new fitting strategy described in the next section.

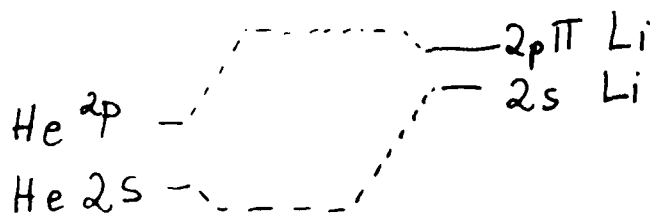
IVb. A strategy to achieve a better fit to the π state of LiHe

As was seen in IVa we did not get an ideal fit in the $R=5$ region as we did not seem to get the fitted curve to be steep enough. It is to be noted that so far we have fitted to Krauss et al. LiHe, π state. It is also to be noted that we have not exhausted, because of lack of computer time, the fit routine and tried to guess the best parameter regions. In this subsection we suggest a new strategy which we plan to carry out in the fall of 1980 when U.S.C. will replenish our computer budget. The strategy is based on the comparison of the shape of the ground LiHe⁺ potential curve (which goes asymptotically to Li⁺ + He) to that of the SCF π LiHe curve (which dissociates properly) as given in the figures in Krauss et al. In this we see the striking fact that the two curves are parallel in the $R=5$ to 6 region and almost parallel at short range; the LiHe has a slightly smaller R_e . This suggests the much of the curve in π LiHe is like the $X^1\Sigma$ LiHe⁺ and this is clearly charge-induced dipole at large distance ($R>4.5$) as it goes at R^{-4} and Li⁺ - Helium repulsion at short distance. Now the former effect is in our model due to the α/r^4 term and the latter in the static and monopole term. (in which e^{-ar} (a chosen so that the term effects the very short range part of the curve only)) is always automatically fit with a negative coefficient). This suggests that as a first run at fitting the π , that we work with the ionic state (a simpler problem) and set our quadrupole term to zero and perhaps again start with the physical value of the polarizability for Helium. This simpler system should be able to be fit. The ionic system then determines the α , its short range cut-off parameters and will give a first guess of the monopole term.

Now we will return to the π Li-He fit, and retain the LiHe^+ parameters as a start. We will then work at large R , $R > 7$ only, fit the quadrupole term and its cut-off parameters. This is suggested again by the 2π state to $X^1\Sigma$ ionic state comparison figure in Krauss where we see that at large R the LiHe system deviates from the ionic system and is less attractive, i.e. the effect of a R^6 comes in. This effect can only be found in the π state as at large R , the Li P state can be reviewed roughly as



i.e. Helium sees a $\{\frac{1}{2}\}$ charge distribution and the $L \pi$ orbit feels the Helium quadrupole moment. The next step will be to now fit again at small R , the monopole term, starting with our ionic result. The small shift must be due to a chemical effect which can be described as:



We should be able to account for this with our monopole parameter.

Hopefully this new strategy will yield a better fit with little computing. The effective potential will then be used to construct the $X^2\Sigma$ state.

Failure in fitting by the procedure of this subsection or in the construction of the Σ state will forebode badly for the ultimate success of this theory.

Figure Captions

Figure 3:

Plot of the electronic energy for the He-Li 2π state calculated according to the method given in section III for various values of the parameter α_d and otherwise always the parameters given in table 1 in section III. The nuclear distance is always $R=3.5$.

Figure 4:

Plot of potential curves for the He-Li 2π state calculated with various parameters for the effective potential and the curve given by Krauss et al. for comparison.

Solid line: result of Krauss et al.

Dotted line: SCF calculation from section III with parameter set p_0

Broken line: calculation with the method given in section IV and

parameter values $\alpha_d = 0.8$
 $\alpha_q = 1.65$
 $\beta = 1.9$
 $c_1 = 4$
 $c_2 = 1.3$
 $c_3 = 0.6$
 $a_0 = -0.8$
 $a_1 = 0$
 $a_2 = 0$
 $a_3 = 0$

Chain line: calculation with the method given in section IV

and parameter values $a_d = 0.9$

$\alpha_q = 1.75$

$a_o = -0.46$

$a_1 = 0$

$\beta = 1.56$

$C_1 = 4$

$a_2 = 0$

$C_2 = 1.3$

$C_3 = 0.6$

$a_3 = 0$

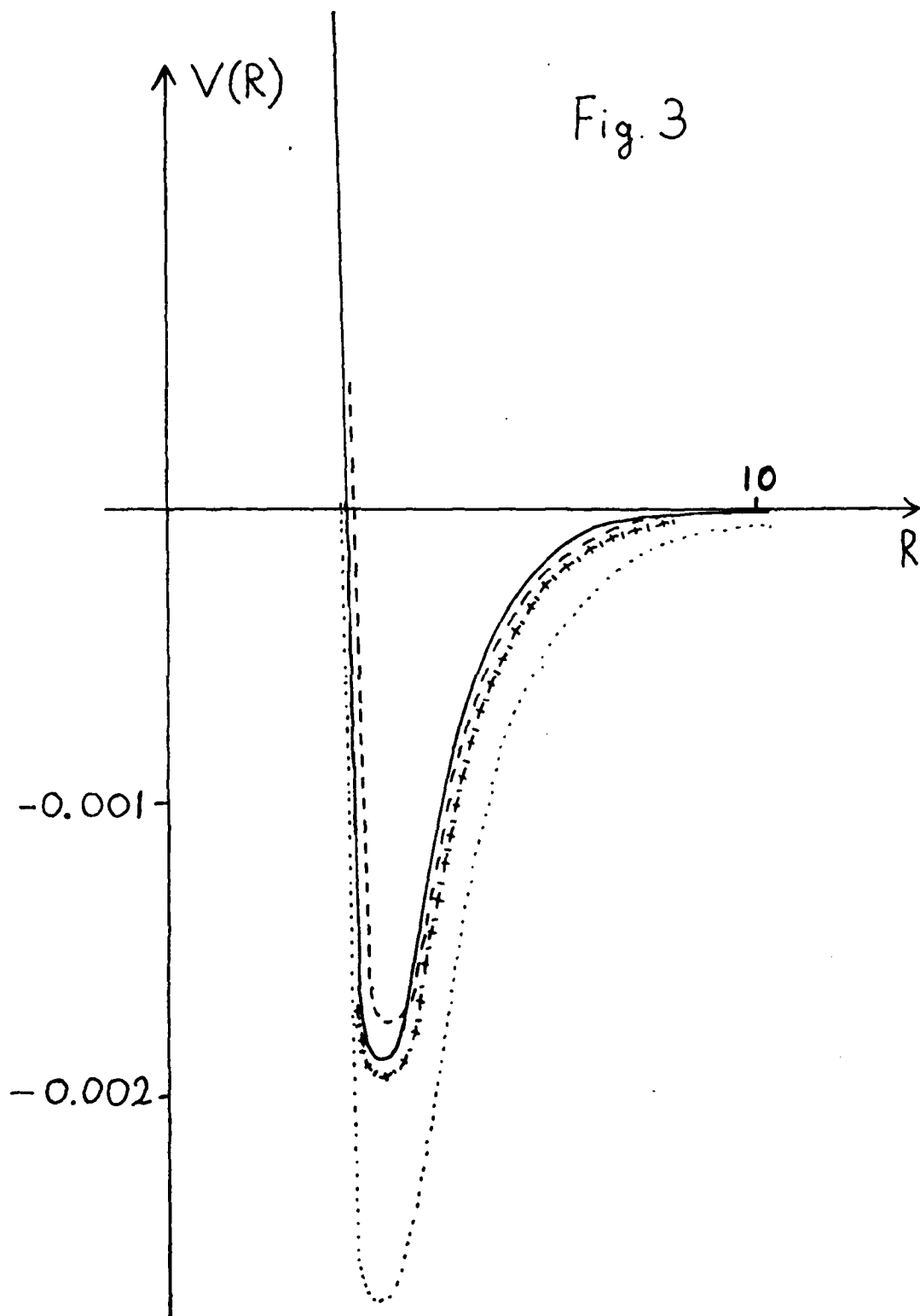
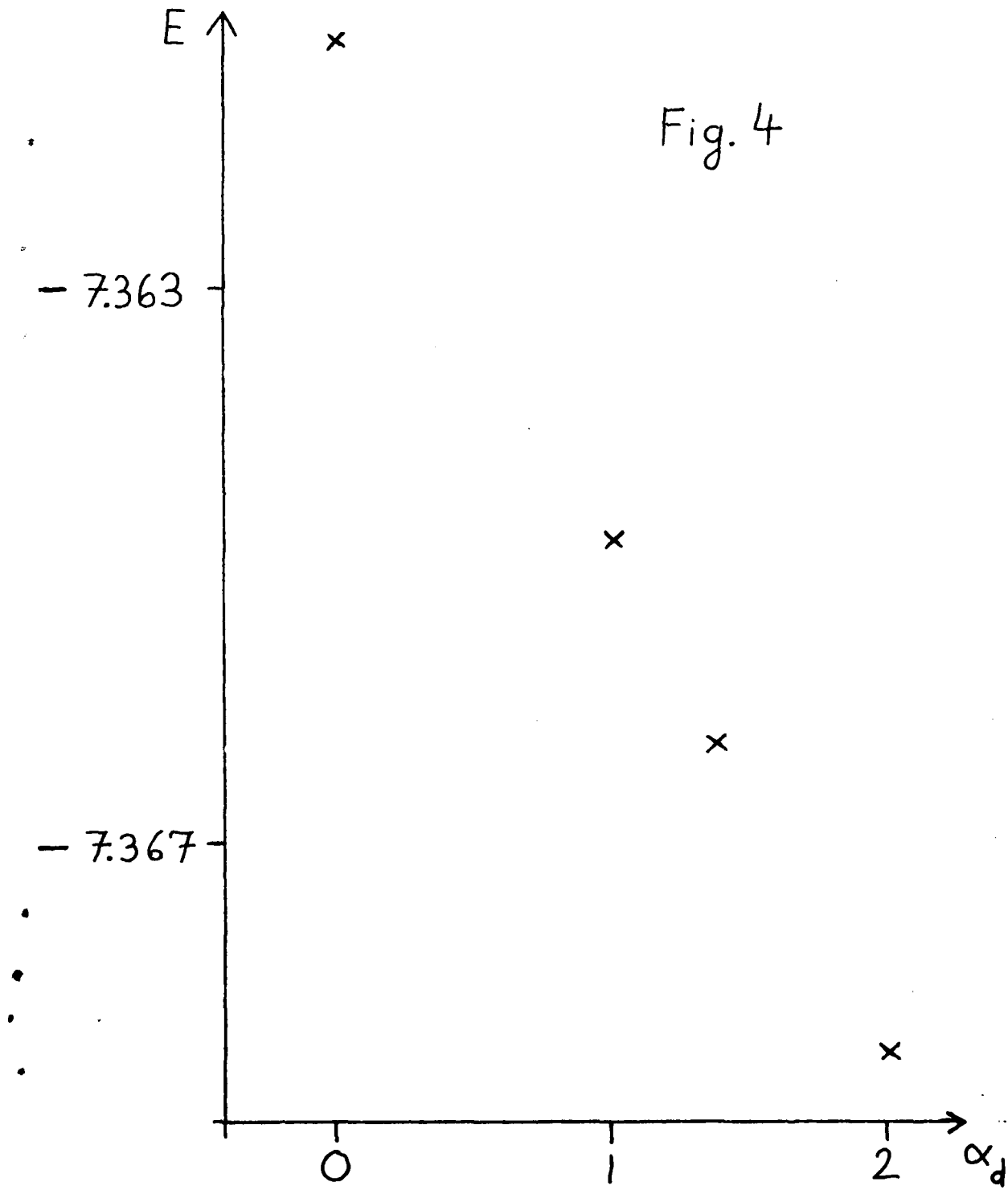


Fig. 4



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Appendix A

Theoretical studies of the low-lying electronic states of GaKr, including extrapolation to InKr and TlKr^{a)}

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We report *ab initio* configuration interaction calculations on the states of the gallium krypton (GaKr) molecule arising from the $\text{Ga}(^2P_{1/2,3/2}, ^2S_{1/2}) + \text{Kr}(^1S_0)$ and $\text{Ga}^+(^1S_0) + \text{Kr}(^1S_0)$ separated atom limits. The potential energy curves for the states arising from the $\text{Ga}(^2P_{1/2,3/2})$ limits, the $1\ 1/2$, $1\ 1/2$, and $1\ 3/2$ states, are found to be repulsive. The potential energy curves for the states arising from the $\text{Ga}(^2S_{1/2})$ and $\text{Ga}^+(^1S_0)$ limits, the $1\ 1/2$ and $1\ 0$ states, are both found to be weakly bound; $D_e(1\ 1/2) = 0.047$ eV and $D(1\ 0) = 0.24$ eV. The potential energy curves and transition moments obtained in the GaKr calculations have been used to simulate the curves and moments for InKr and TlKr. Using this data the absorption and emission coefficients of all three molecules have been calculated.

I. INTRODUCTION

The Group IIIA-rare gas excimer molecules are considered to be attractive candidates for developing an efficient, high power, tunable laser in the visible region of the spectrum.¹ The transition under consideration is a perturbed $(n+1)^2S_{1/2} - n^2P_{1/2,3/2}$ transition of the Group IIIA atom. While current experimental studies have concentrated on the thallium-rare gas systems, especially TlXe, as the most promising candidates, Gallagher² has recently raised the possibility of using the gallium-rare gas systems by obtaining gallium atoms from the dissociation of GaI_3 .

To provide further information on the nature of the excimer states involved in these studies, we report here *ab initio* configuration interaction calculations on a prototype Group IIIA-rare gas diatomic molecule, GaKr. We present the potential energy curves for all of the states arising from the neutral $\text{Ga}(^2P_{1/2,3/2}, ^2S_{1/2}) + \text{Kr}(^1S_0)$ and ionic $\text{Ga}^+(^1S_0) + \text{Kr}(^1S_0)$ separated atom limits and the dipole transition moments radiatively coupling the states. We then use the computed potential curves and transition moments for GaKr, along with the experimental atomic spin-orbit coupling constants, to model the curves and moments for InKr and TlKr. With this data we calculate the emission and absorption coefficients for all three systems using the classical technique developed by Gallagher and co-workers.¹⁶

II. ELEMENTARY THEORETICAL CONSIDERATIONS

Let us first consider the description of the states of the Group IIIA-rare gas molecules without spin-orbit corrections. The valence $\text{Ga}(^2P) + \text{Kr}(^1S)$ separated atom limit gives rise to a $^2\Pi$ state and a $^2\Sigma^+$ state, the Rydberg $\text{Ga}(^2S) + \text{Kr}(^1S)$ limit gives rise to another $^2\Sigma^+$ state

and the ionic $\text{Ga}^+(^1S) + \text{Kr}(^1S)$ limit gives rise to a $^1\Sigma^+$ state. We will label the states which arise from the valence limit the $1^2\Pi$ and $1^2\Sigma^+$ states, that from the Rydberg limit the $2^2\Sigma^+$ state and that from the ionic limit the $1^1\Sigma^+$ state.

The orbital diagrams for the $1^2\Pi$, $1^2\Sigma^+$, and $1^1\Sigma^+$ states of a Group IIIA-rare gas molecule are given in Fig. 1. From these diagrams it is evident that none of the resulting potential energy curves are expected to be chemically bound. In the ionic state, however, weak binding can result from the charge-induced dipole interaction of the Group IIIA ions and the rare gas atoms. In fact, this interaction might also be expected to give rise to a weak binding in the $2^2\Sigma^+$ state. Since the Rydberg orbital of the Group IIIA atom is diffuse, the approaching rare gas atom can easily polarize the Rydberg orbital out of the

THE LOW-LYING ELECTRONIC STATES
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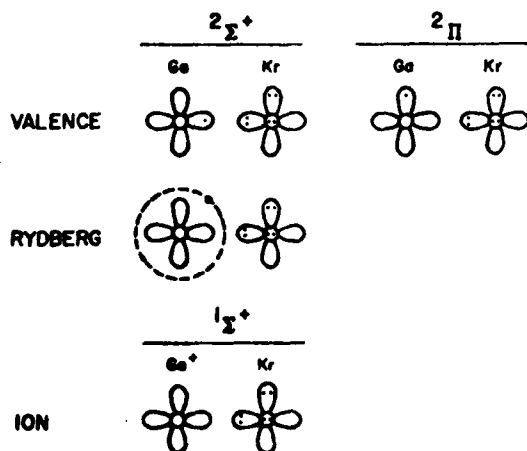


FIG. 1. Orbital diagrams for the low-lying electronic states of GaKr and GaKr^+ . The two lobed figures represent 4p orbitals in the plane of the paper; the circle represents a 4p orbital perpendicular to the plane of the paper; the 5s Rydberg orbital is represented by a large dashed circle.

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interatomic region, thus partially unshielding the Group IIIA ionic core. The binding in the $2^3\Sigma^+$ state should, of course, be substantially less than that in the $1^1\Sigma^+$ state.

For the valence states the repulsiveness of the curves should be roughly proportional to the number of po electrons since the overlap of the two atomic charge distributions is dominated by the overlap of the po orbitals. Thus, the potential curve for the $1^3\Pi$ state with two po electrons should be less repulsive than that for the $1^2\Sigma^+$ state with three po electrons.

As we shall later see, at short internuclear separations the energies of the $1^2\Sigma^+$ and $2^2\Sigma^+$ states are nearly equal and there is a strong interaction between the two states. This mixing is strong in spite of the fact that one state is a valence state and the other a Rydberg state because the two zero-order configurations (see the next section) differ by only a single excitation.

A complete treatment of the electronic states of the Group IIIA-rare gas molecules must include the effects of spin-orbit coupling. Using the simple model developed in earlier papers for including the effects of spin-orbit coupling in diatomic molecules,³ only the $1^3\Pi$ and $1^2\Sigma^+$ states are affected by the spin-orbit interaction, and the coupling arises solely from the spin-orbit interaction in the Group IIIA atom. For gallium the $^2P_{1/2}$ - $^2P_{3/2}$ splitting is only 0.10 eV⁴; however, by thallium this splitting has increased to 0.97 eV.⁴

In a molecule only the z component of the total angular momentum,

$$\Omega = \Lambda + S_z,$$

is a good quantum number. Thus, from the $\text{Ga}(^2P_{1/2,3/2}) + \text{Kr}(^1S_0)$ separated atom limits we obtain two $\Omega = 1/2$ states and one $\Omega = 3/2$ state (the $I\ 1/2$, $II\ 1/2$, and $III\ 3/2$ states), from the $\text{Ga}(^2S_{1/2}) + \text{Kr}(^1S_0)$ limit another $\Omega = 1/2$ state (the $III\ 1/2$ state), and from the $\text{Ga}(^1S_0) + \text{Kr}(^1S_0)$ limit an $\Omega = 0$ state (the $I\ 0$ state). At large internuclear distances the $I\ 3/2$ and $II\ 1/2$ potential curves are degenerate and are separated from the $I\ 1/2$ (ground state) curves by the group IIIA $^2P_{3/2}$ - $^2P_{1/2}$ splitting. As the distance decreases the $1^3\Pi$ and $1^2\Sigma^+$ curves rapidly separate, the separation increasing approximately exponentially. As a result at short distance the atomic spin-orbit coupling is nearly quenched and the $I\ 1/2$ and $II\ 3/2$ curves approximate the $1^3\Pi$ curve and the $II\ 1/2$ curve approximates the $1^2\Sigma^+$ curve. The potential curves of the $2^3\Sigma^+$ ($III\ 1/2$) and $1^1\Sigma^+$ ($I\ 0$) states are unaffected by the inclusion of spin-orbit coupling.

III. DETAILS OF THE CALCULATIONS

A. Basis sets

The calculations employed an atomic ($14s11p5d$) primitive Gaussian basis set for both the gallium and krypton atoms.⁵ The core orbitals ($1s, 2s, 3s, 2p, 3p$, and $3d$) were contracted to a single function while the valence orbitals ($4s$ and $4p$) were contracted to two functions using the general contraction method of Raffenetti⁶ (see also Ref. 7). These atomic basis sets were augmented

with a single set of $3d$ functions, $\zeta_{0d} = 0.16$ and $\zeta_{4d} = 0.35$, to describe molecular polarization effects. The values of these exponents were based on calculations on other excimer laser systems.^{3,8}

Since the transition of interest involves the first Rydberg state of the gallium atom, the gallium basis set was augmented with two diffuse s functions, $\zeta_s = 0.026$ and 0.011 , and a diffuse p function, $\zeta_p = 0.010$, to describe this state. The exponents of these functions were obtained from Hartree-Fock (HF) calculations on the 2S and 2P Rydberg states of the gallium atom.

The final basis sets thus consisted of a ($18s12p6d$) primitive set contracted to [$7s5p2d$] for gallium and a ($14s11p6d$) primitive set contracted to [$5s4p2d$] for krypton.

B. Calculations on the gallium atom

The reference orbitals for the configuration interaction (CI) calculations on the gallium atom were obtained from a Hartree-Fock (HF) calculation of the 2P state of the atom with the configuration

$$^2P: \dots 4s^2 4p. \quad (1)$$

(The $4p$ set includes all three cartesian components and all are equivalent.) The Rydberg $5s$ orbital was obtained from an IVO calculation⁹ using the $4s^2$ core. In terms of these orbitals the reference configurations for the other states of interest are

$$^2S: \dots 4s^2 5s \quad (2)$$

$$^1S: \dots 4s^2. \quad (3)$$

Both polarization CI (POL-CI)¹⁰ and full CI calculations have been carried out on the above states of the gallium atom. The POL-CI calculations include all single and double excitations relative to configurations (1)-(3) with the restrictions that

(1) all core orbitals ($1s-3s$, $2p-3p$, and $3d$) remain doubly occupied and

(2a) no more than one electron occupy the Rydberg $5s$ and virtual orbitals (2P and 1S states) or

(2b) no more than one electron occupy the Rydberg $5s$ orbital and no more than one electron occupy the virtual orbitals (2S state).

The POL-CI calculations involve 22 space and 33 space/spin configurations for the 2P state, 27 space and 43 space/spin configurations for the 2S state, and 15 space and 15 space/spin configurations for the 1S state.¹¹ Note that the POL-CI wavefunction accounts for the $4s^2-4p^2$ near-degeneracy effect.

The less restrictive condition, (2b), for the 2S state is necessary to obtain a comparable description of this state. Only by relaxing condition (2a) can configurations such as

$$\dots [4pnp]5s$$

be included in the POL-CI wavefunction of the 2S state. These configurations account for the first-order difference between the $4p$ orbital obtained from the calcula-

tions on the 2P state and the p orbital needed to describe the angular correlation of the $4s^2$ pair ($4s-4p$ near degeneracy) and are quite important. Comparable configurations are automatically included in the POL-CI wavefunctions of the 2P and 1S states.

The full CI calculations include all excitations (single-triple) relative to the configurations (1)–(3) with only restriction (1) above. The full CI calculations include 157 space and 263 space/spin configurations for the 2P state, 204 space and 306 space/spin configurations for the 2S state, and 42 space and 42 space/spin configurations for the 1S state.¹¹ Within the frozen core approximation the accuracy of the results obtained from the full CI calculations is only limited by the completeness of the basis set.

C. Hartree-Fock calculations on GaKr

The *reference orbitals* for the POL-CI calculations¹⁰ on the GaKr molecule were obtained from an HF calculation on the $1^2\Sigma^+$ state with configuration¹²

$$\dots 13\sigma^2 14\sigma^2 15\sigma^2 16\sigma^2 7\pi^4 \quad (1a)$$

In the POL-CI calculations the core orbitals (12 σ orbitals, 12 π orbitals, and 4 δ orbitals) are always required to be doubly occupied and so it is convenient to renumber the *valence orbitals* so that (1a) becomes

$$1^2\Sigma^+: 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 \quad (1b)$$

As $R \rightarrow \infty$ the above orbitals become

$$1\sigma - 4s_{Kr} \quad 1\pi - 4p_{Kr}$$

$$2\sigma - 4p\sigma_{Kr}$$

$$3\sigma - 4s_{Ga}$$

$$4\sigma - 4p\sigma_{Ga}$$

The IVO method,⁹ with a $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$ core, was used to generate the *valence* 2π and *Rydberg* 5σ orbitals. As $R \rightarrow \infty$ these orbitals become the $4p\pi$ and $5s$ orbitals of the gallium atom. The virtual orbitals were also obtained from the IVO calculations.

In terms of the orbitals defined in this way the *reference configurations* for the other states of interest are¹²

$$1^2\Pi: 1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 2\pi \quad (2)$$

$$2^2\Sigma^+: 1\sigma^2 2\sigma^2 3\sigma^2 5\sigma^2 1\pi^4 \quad (3)$$

$$1^1\Sigma^+: 1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 \quad (4)$$

D. Polarization configuration interaction calculations on GaKr

The POL-CI calculations¹⁰ on GaKr included all single and double excitations relative to the reference configurations given above with the restrictions that

(1) all core orbitals remain doubly occupied and

(2a) no more than one electron occupy the Rydberg 5σ and virtual orbitals ($^2\Pi$ and $^1\Sigma^+$ states) or

(2b) no more than one electron occupy the Rydberg 5σ orbital and no more than one electron occupy the virtual orbitals ($^2\Sigma^+$ states).

For the $^2\Sigma^+$ states the calculations considered both states simultaneously. This procedure results in 556 space and 1565 space/spin configurations for the $^2\Pi$ states, 764 space and 2314 space/spin configurations for the $^2\Sigma^+$ states, and 368 space and 558 space/spin configurations for the $^1\Sigma^+$ state.

The less restrictive condition, (2b), is necessary for the $^2\Sigma^+$ states to allow for configurations such as

$$1\sigma^2 2\sigma^2 [2\pi n\pi] 5\sigma 1\pi^4,$$

which are important in the description of the Rydberg $^2\Sigma^+$ state. As was the analogous case in the gallium atom, these configurations are necessary to allow for the inclusion of the $4s^2-4p^2$ near-degeneracy effect in the molecular wavefunction.

E. Inclusion of spin-orbit coupling in GaKr

As in our earlier calculations on excimer systems,^{3,13} we have adopted a simple model³ for including the effects of spin-orbit coupling on the calculated potential energy curves and wavefunctions. The experimental spin-orbit parameters for the open-shell atom, gallium in the present case, are used to determine the matrix elements of the spin-orbit Hamiltonian, H_{so} , coupling the molecular states at $R = \infty$. These matrix elements are then assumed to be independent of R and are added to the diagonal matrix of the electronic energies

$$H^0(R) = \delta_{ij} E_i(R) + H_{so} \quad (5)$$

The energies and wavefunctions with spin-orbit corrections are obtained by diagonalizing $H^0(R)$. This procedure is reasonable only so long as (1) the molecular states retain the identity of the atomic states from which they arise and (2) the atomic contributions to the molecular spin-orbit interactions are dominant.

For GaKr the spin-orbit interaction affects only those states which arise from the $Ga(^2P) + Kr(^1S)$ limit. The Hamiltonian matrix for the $\Omega = 1/2$ states arising from this limit is

$$H^{\Omega=1/2} = \begin{bmatrix} E(1^2\Sigma^+) & \sqrt{2}\lambda_{\sigma\pi} \\ \sqrt{2}\lambda_{\sigma\pi} & E(1^2\Pi) - \lambda_{\sigma\pi} \end{bmatrix} \quad (6a)$$

and for the $\Omega = 3/2$ state is

$$H^{\Omega=3/2} = E(1^2\Pi) + \lambda_{\sigma\pi} \quad (6b)$$

In (6) $\lambda_{\sigma\pi}$ is one third of the $^2P_{3/2}-^2P_{1/2}$ splitting in the gallium atom. The energies of the $2^2\Sigma^+$ and $1^1\Sigma^+$ states of GaKr are unaffected by the inclusion of spin-orbit coupling. The wavefunctions for the states obtained by diagonalizing (6) may be written in the form

$$|I 1/2\rangle = \cos\theta |1^2\Pi, \beta\rangle + \sin\theta |1^2\Sigma^+, \alpha\rangle \quad (7a)$$

$$|II 1/2\rangle = -\sin\theta |1^2\Pi, \beta\rangle + \cos\theta |1^2\Sigma^+, \alpha\rangle \quad (7b)$$

$$|I 3/2\rangle = |1^2\Pi, \sigma\rangle, \quad (7c)$$

where θ is the spin rotation angle. The wavefunctions for the $||I 1/2\rangle$ and $|I 0\rangle$ states are

$$|III 1/2\rangle = |2^2\Sigma^+, \alpha\rangle \quad (7d)$$

$$|I 0\rangle = |1^1\Sigma^+, \gamma\rangle \quad (7e)$$

TABLE I. Calculations on the 2P , 2S , and 1S (ion) states of Ga and the 1S state of krypton. For Ga the experimental results have been corrected for spin-orbit effects (see the text). Units are as indicated.

Atom state	2P	Ga(Ga $^+$) 2S	1S	Kr 1S
Total energies (hartree) ^a				
POL-CI	0.22523	0.12130	0.01912	0.97377 ^b
Full CI	0.23484	0.12750	0.02305	...
Excitation energies (eV)				
POL-CI	0.00	2.83	5.61	...
Full CI	0.00	2.92	5.76	...
Expt'l ^c	0.000	3.005	5.930	...
Transition moment (ea_0)				
POL-CI	...	-1.298 ^d
Lifetimes (nsec)				
POL-CI	...	8.2 ^e
Expt'l	...	6.8 ^f

^aFor Ga the energies are relative to -1923 hartree; for Kr the energies are relative to -2751 hartree.

^bFor Kr the POL-CI wavefunction is equivalent to the HF wavefunction.

^cReference 4.

^dThis is the matrix element $1/3[\langle ^2S|x|^2P_x\rangle + \langle ^2S|y|^2P_y\rangle + \langle ^2S|z|^2P_z\rangle]$.

^eUsing the experimental excitation energy we obtain 6.9 nsec.

^fReference 14.

With the definitions (7) the dipole transition moments coupling the $III\ 1/2$ state with all of the lower states are

$$\mu_z(III\ 1/2 - I\ 1/2) = \sin\theta \langle ^2\Sigma^+ | z | ^1\Sigma^+ \rangle \quad (8a)$$

$$\mu_x(III\ 1/2 - I\ 1/2) = \cos\theta \langle ^2\Sigma^+ | x | ^1\Pi_u \rangle / \sqrt{2} \quad (8b)$$

$$\mu_z(III\ 1/2 - II\ 1/2) = -\cos\theta \langle ^2\Sigma^+ | z | ^1\Sigma^+ \rangle \quad (9a)$$

$$\mu_x(III\ 1/2 - II\ 1/2) = \sin\theta \langle ^2\Sigma^+ | x | ^1\Pi_u \rangle / \sqrt{2} \quad (9b)$$

$$\mu_z(III\ 1/2 - I\ 3/2) = -\langle ^2\Sigma^+ | z | ^1\Pi_u \rangle / \sqrt{2} \quad (10)$$

Since the $\langle ^2\Sigma^+ | x | ^1\Pi_u \rangle$ transition moment is expected to be comparable in magnitude to the $\langle ^2\Sigma^+ | z | ^1\Sigma^+ \rangle$ moment (at $R=\infty$ they are identical), it is clear from (8) and (9) that the transitions from the $III\ 1/2$ state of the $I\ 1/2$ and $II\ 1/2$ states can have both large parallel and perpendicular components.

IV. RESULTS FOR Ga, GaKr, AND GaKr $^+$

A. Electronic states of Ga, without spin-orbit corrections

The results of the calculations on the Ga atom are summarized in Table I. The computed 2S - 2P excitation energy is 2.83 eV (POL-CI) and 2.92 eV (full CI). Averaging the multiplet energies for the $^2P_{1/2}$ and $^2P_{3/2}$ states of gallium from Moore,⁴ the experimental 2S - 2P splitting is calculated to be 3.005 eV, just 0.08-0.17 eV larger than the computed spacing. The errors in the calculated ionization potentials, 5.61 eV (POL-CI) and 5.76 eV (full CI), are somewhat larger, being 0.32 and 0.17 eV, respectively.

The lifetime of the 2S state of gallium has been determined by Norton and Gallagher¹⁴ to be 6.8 ± 0.3 nsec. For the model used here the lifetime of the 2S state is independent of the spin-orbit corrections. From the POL-CI wavefunctions we calculate a lifetime of 8.2 nsec for the 2S state (6.9 nsec, if the experimental excitation energy is used instead of the calculated excitation energy).

B. Electronic states of GaKr and GaKr $^+$, without spin-orbit corrections

The energies of the $1^2\Pi$, $1,2^2\Sigma^+$, and $1^1\Sigma^+$ states of GaKr and GaKr $^+$ obtained from the POL-CI calculations are listed in Table II and the resulting potential energy curves are plotted in Fig. 2. As is usual in such calculations,^{3,6,13} the energies of the $1^2\Pi$ and $1^2\Sigma^+$ states, both of which arise from the 2P limit, are not exactly equal at $R=15.0a_0$ (the largest value of R considered). The difference, 0.00114 hartree (0.031 eV), is attributable to the inequivalence of the $4p\sigma$ and $4p\pi$ orbitals and to core polarization effects (the core orbitals were obtained from HF calculations on the $1^2\Sigma^+$ state which does not have the full rotational symmetry of the atom). In the plots the asymptotic energies of the states have been adjusted to give the experimental atomic energy splittings.

In line with the discussion in Sec. II, the potential energy curve for the $1^2\Pi$ state is found to be less repulsive than that of the $1^2\Sigma^+$ state, thus making the $1^2\Pi$ state the ground state of the system. In fact, we find that the $1^2\Pi$ curve is slightly bound, $D_e \sim 0.04$ eV (see Table III). Although spurious minima have been found in previous calculations on excimer systems^{8,13} and attributed to basis set limitations, the well in the $1^2\Pi$ curve is substantially larger than has been observed heretofore. We thus suspect that the minimum in the $1^2\Pi$ curve is not just a result of calculational limitations. The depth of the well in the real $1^2\Pi$ curve is, of course, expected to be significantly larger than that calculated here since the POL-CI method is not designed to account for the attractive van der Waals' interaction.

As predicted in Sec. II both the $2^2\Sigma^+$ and $1^1\Sigma^+$ curves

TABLE II. Energies obtained from the POL-CI calculations on the low-lying electronic states of GaKr and GaKr $^+$. Distances are in bohr; energies are in hartree. Energies are relative to -4674 hartree.

R	$1^2\Pi$	GaKr $1^2\Sigma^+$	$2^2\Sigma^+$	GaKr $^+$ $1^1\Sigma^+$
3.75	-1.02539	-0.96866	-0.93379	-0.85625
4.00	-1.07933	-1.01870	-0.99238	-0.90683
4.50	-1.14810	-1.08688	-1.06440	-0.96758
5.00	-1.17924	-1.13516	-1.08855	-0.99287
5.50	-1.19225	-1.16324	-1.09545	-1.00070
6.00	-1.19772	-1.17938	-1.09677	-1.00202
6.50	-1.19984	-1.18865	-1.09631	-1.00107
7.00	-1.20045	-1.19396	-1.09545	-0.99950
8.00	-1.20020	-1.19865	-1.09420	-0.99670
10.00	-1.19833	-1.20029	-1.09406	-0.99402
15.00	-1.18878	-1.20012	-1.09502	-0.99304

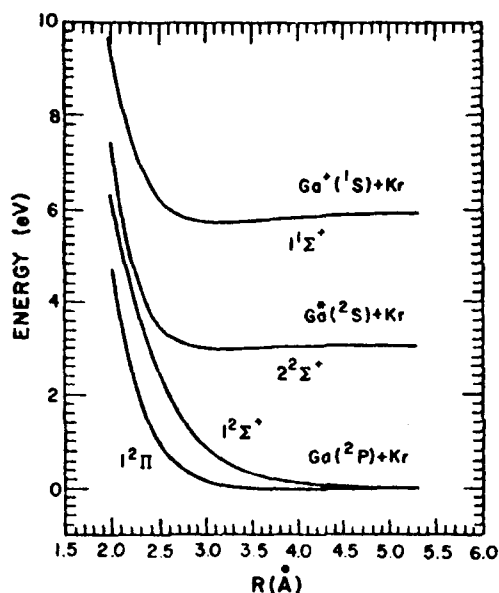
THE LOW-LYING STATES OF GaKr AND GaKr⁺

FIG. 2. Calculated potential energy curves for the states of GaKr and GaKr⁺ arising from the Ga(2P, 2S) + Kr(1S) and Ga(1S) + Kr(1S) separated atom limits. The curves have been uniformly shifted to correct for the errors in the gallium atom excitation energies.

are found to be bound with calculated dissociation energies of 0.047 and 0.24 eV, respectively. Again, inclusion of the attractive van der Waals' interaction would be expected to significantly increase the calculated well depths. There is a slight hump in the calculated potential curve of the 2²Σ⁺ state, ~0.026 eV, since the long-range interaction of the excited Ga and Kr atoms is repulsive. This hump could, however, disappear when the van der Waals' attraction is added to the calculated curve.

The dipole transition moments radiatively coupling the states of GaKr are given in Table IV and plotted in Fig. 3. At $R = \infty$ the transition moment coupling the 1²Π and 1²Σ⁺ states is identically zero and those coupling the (1²Π, 1²Σ⁺) states with the 2²Σ⁺ state are approximately equal to the 2S-2P atomic transition moment (after properly accounting for differences in degeneracy

TABLE III. Spectroscopic constants for the bound states of ⁶⁹Ga⁸⁴Kr and ⁶⁹Ga⁸⁴Kr⁺. Units are as indicated.

	GaKr		GaKr ⁺
	1 ² Π	2 ² Σ ⁺	1 ² Σ ⁺
T_e , eV	0.00	2.82	5.40
R_e , Å	3.78	3.17	3.14
D_e , eV	0.041	0.047	0.24
ω_e , cm ⁻¹	36	66	83
B_e	0.0312	0.0442	0.0452

TABLE IV. Dipole transition moments coupling the low-lying states of GaKr obtained from the POL-CI calculations.

R	1 ² Σ ⁺ -1 ² Π ^a	2 ² Σ ⁺ -1 ² Π ^a	2 ² Σ ⁺ -1 ² Σ ⁺
3.75	-0.9037	-0.7877	0.4095
4.00	-0.8462	-0.8680	-0.3055
4.50	-0.1365	-1.2090	-2.0676
5.00	0.0992	-1.2349	-1.4402
5.50	0.1257	-1.2469	-1.2456
6.00	0.1166	-1.2554	-1.1893
6.50	0.0984	-1.2619	-1.1800
7.00	0.0789	-1.2677	-1.1902
8.00	0.0476	-1.2777	-1.2310
10.00	0.0163	-1.2898	-1.2976
15.00	0.0018	-1.2917	-1.3101

^aThe matrix element given is $\langle \pi^2 \Sigma^+ | x | 1^2 \Pi \rangle$.

factors). As R decreases rather minor changes occur until $R \sim 2.5$ Å. For $R < 2.5$ Å substantial changes are noted in all of the transition moments, although the change in the 2²Σ⁺-1²Π moment is less dramatic than for the 2²Σ⁺-1²Σ⁺ and 1²Σ⁺-1²Π moments. The erratic behavior of the transition moments for $R < 2.5$ Å is one manifestation of the strong interaction of the 1²Σ⁺ and 2²Σ⁺ states at short R .

Although, as noted above, substantial changes are found in the transition moments for $R < 2.5$ Å, such behavior can be expected to have little effect on the observable properties of the system. At $R = 2.5$ Å the energy of the 2²Σ⁺ state is >0.5 eV above its asymptote so that the region $R < 2.5$ Å would be thermally inaccessible.

DIPOLE TRANSITION MOMENTS AMONG THE LOW-LYING STATES OF GaKr

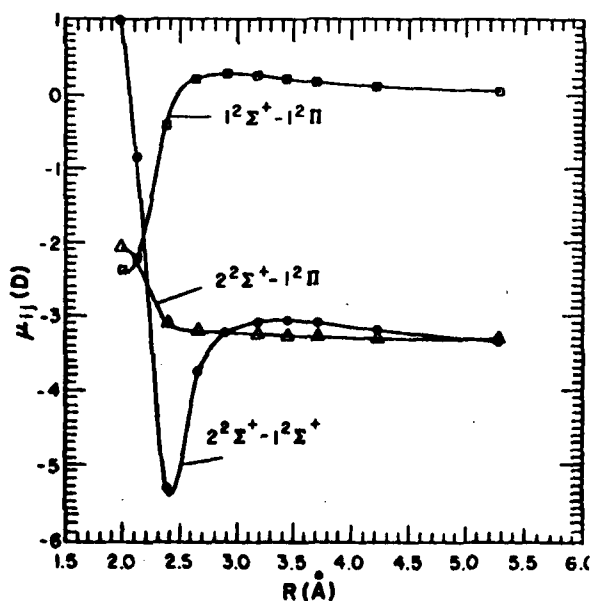


FIG. 3. Calculated dipole transition moments for the 1²Σ⁺-1²Π, 2²Σ⁺-1²Π, and 2²Σ⁺-1²Σ⁺ transitions in GaKr.

THE LOW-LYING STATES OF GaKr AND GaKr⁺ WITH SPIN-ORBIT CORRECTIONS

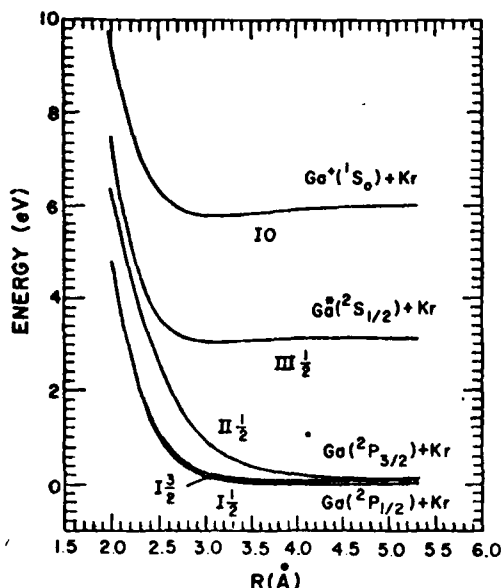


FIG. 4. Calculated potential energy curves for the states of GaKr and GaKr⁺ arising from the Ga(²P_{1/2}, ³/₂, ²S_{1/2}) + Kr(¹S₀) and Ga⁺(¹S₀) + Kr(¹S₀) separated atom limits. The curves have been uniformly shifted to correct for the errors in the gallium excitation energies.

C. Electronic states of GaKr and GaKr⁺, with spin-orbit corrections

The energies of the states of GaKr and GaKr⁺ with spin-orbit corrections are given in Table V and the resulting potential energy curves are plotted in Fig. 4. In calculating the spin-orbit corrected energies we shifted the ¹Σ⁺ energies to agree with the ¹Σ⁺ energy at the largest value of *R* considered (*R* = 15.0 *a*₀). Again, in plotting the potential energy curves, the asymptotic energies of the states have been adjusted to give the correct atomic energy splittings.

As predicted in Sec. II, at short *R* the curves for the

TABLE V. Calculated energies of the *I* 1/2, *II* 1/2, and *I* 3/2 states of GaKr with spin-orbit corrections. Distances are in bohr; energies are in hartree. Energies are relative to the energy of the ¹Σ⁺ state at *R* = 15 *a*₀.

<i>R</i>	<i>I</i> 1/2	<i>I</i> 3/2	<i>II</i> 1/2
3.75	0.17228	0.17484	0.23152
4.00	0.11835	0.12091	0.18147
4.50	0.04957	0.05213	0.11329
5.00	0.01841	0.02099	0.06502
5.50	0.00538	0.00799	0.03698
6.00	-0.00015	0.00252	0.02089
6.50	-0.00234	0.00040	0.01170
7.00	-0.00307	-0.00022	0.00650
8.00	-0.00316	0.00003	0.00215
10.00	-0.00280	0.00090	0.00103
15.00	-0.00251	0.00126	0.00126

TABLE VI. Calculated dipole transition moments coupling the *III* 1/2 and *I* 1/2, *II* 1/2 and *I* 3/2 states of GaKr with spin-orbit corrections. Distances are in bohr; moments are in atomic units.

<i>R</i>	<i>III</i> 1/2- <i>I</i> 1/2		<i>III</i> 1/2- <i>II</i> 1/2		<i>III</i> 1/2- <i>I</i> 3/2	
	<i>z</i>	(<i>x</i> , <i>y</i>)	<i>z</i>	(<i>x</i> , <i>y</i>)	(<i>x</i> , <i>y</i>)	(<i>x</i> , <i>y</i>)
4.00	-0.0086	0.6135	-0.3054	-0.0173	-0.6138	
4.50	-0.0576	0.8545	-2.0667	-0.0238	-0.8549	
5.00	-0.0549	0.8726	-1.4392	-0.0333	-0.8732	
5.50	-0.0701	0.8803	-1.2437	-0.0496	-0.8817	
6.00	-0.1007	0.8845	-1.1850	-0.0752	-0.8877	
6.50	-0.1504	0.8850	-1.1704	-0.1138	-0.8923	
7.00	-0.2249	0.8803	-1.1688	-0.1694	-0.8964	
8.00	-0.4405	0.8436	-1.1495	-0.3233	-0.9035	
10.00	-0.7254	0.7562	-1.0759	-0.5098	-0.9120	
15.00	-0.7564	0.7457	-1.0697	-0.5273	-0.9134	

I 1/2 and *I* 3/2 states become nearly degenerate and just represent the curves for the two spin-orbit components of the ¹Σ⁺ state. Also, at short *R* the *II* 1/2 curve closely approximates the curve for the ¹Σ⁺ state. The potential energy curves for the ²Σ⁺ (*III* 1/2) and ¹Σ⁺ (*I* 0) states are unchanged by the inclusion of spin-orbit corrections.

The dipole transition moments radiatively coupling the states of GaKr with spin-orbit corrections are given in Table VI and are plotted in Fig. 5. It should be noted that both the *z* component of the *III* 1/2-*I* 1/2 transition and the *x* component of the *III* 1/2-*II* 1/2 transition are now found to vary significantly even for *R* > 2.5 Å. This is due to the changing nature of the *I* 1/2 and *II* 1/2 states

DIPOLE TRANSITION MOMENTS AMONG THE LOW-LYING STATES OF GaKr WITH SPIN-ORBIT CORRECTIONS

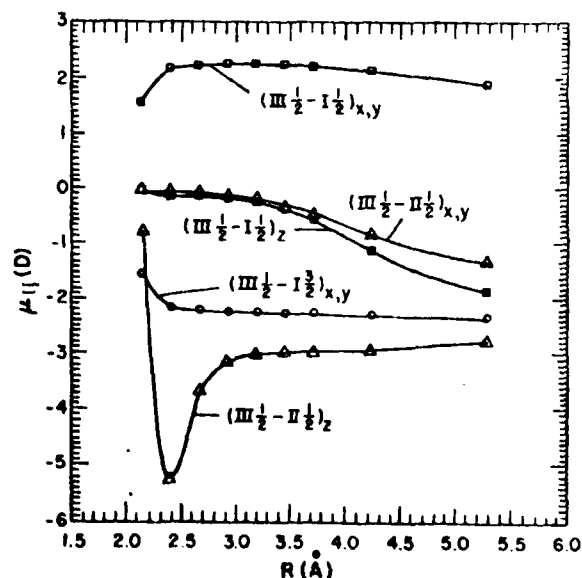


FIG. 5. Calculated dipole transition moments for the *III* 1/2-*I* 1/2, *III* 1/2-*I* 3/2, and *III* 1/2-*II* 1/2 transitions in GaKr.

TABLE VII. Excitation energies and ionization potentials for the Ga, In, and Tl atoms, in eV. Taken from Ref. 4.

Group IIIA atoms			
State	Ga	In	Tl
$^2P_{1/2}$	0.000	0.000	0.000
$^2P_{3/2}$	0.102	0.274	0.966
$^2S_{1/2}$	3.073	3.022	3.282
1S_0	5.998	5.786	6.108

as the atomic spin-orbit coupling is quenched by molecular formation.

V. EXTRAPOLATION TO InKr AND TlKr

To provide information on the InKr and TlKr molecules, the latter being the most experimentally accessible of the Group IIIA-krypton molecules, the potential curves for InKr and TlKr have been estimated from the GaKr curves. The excitation energies and ionization potentials for the series Ga, In, and Tl are given in Table VII. As can be seen, this series does not form a steady progression: In has a lower ionization potential and excitation energies than Ga, as expected, but Tl has a higher ionization potential and excitation energies. This anomalous behavior in Tl is due in part to the filling of the 4f shell ("lanthanide contraction") and to the larger spin-orbit interactions.¹⁵ These effects are only partially accounted for in the present models.

To simulate InKr and TlKr, the experimental spin-

THE LOW-LYING STATES OF InKr AND InKr⁺ WITH SPIN-ORBIT CORRECTIONS

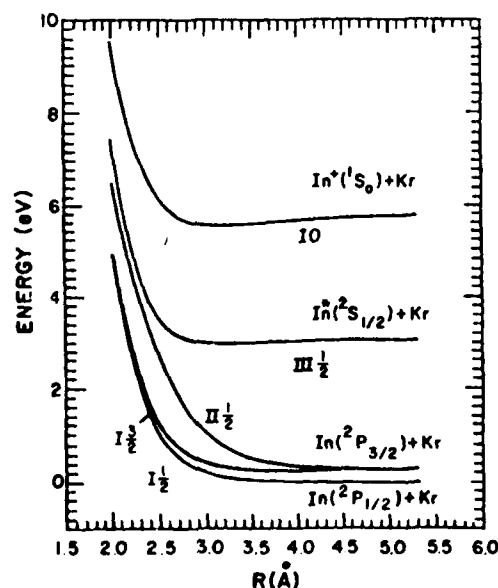


FIG. 6. Model potential energy curves for the states of InKr and InKr⁺ arising from the $\text{In}(^2P_{1/2, 3/2}) + \text{Kr}(^1S_0)$ and $\text{In}(^1S_0) + \text{Kr}(^1S_0)$ separated atom limits, see the text.

THE LOW-LYING STATES OF TlKr AND TlKr⁺ WITH SPIN-ORBIT CORRECTIONS

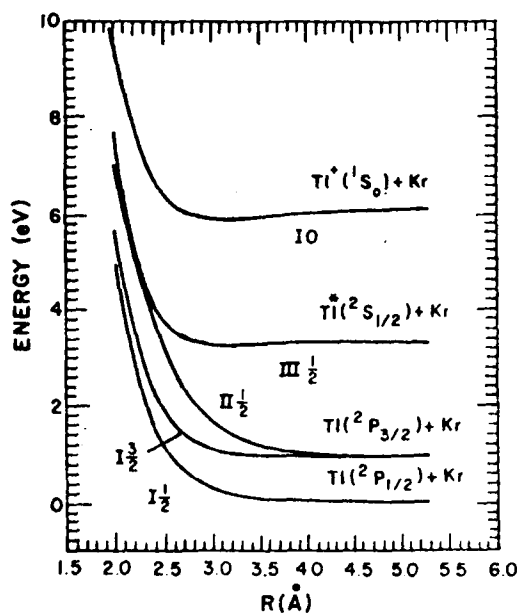


FIG. 7. Model potential energy curves for the states of TlKr and TlKr⁺ arising from the $\text{Tl}(^2P_{1/2, 3/2}) + \text{Kr}(^1S_0)$ and $\text{Tl}(^1S_0) + \text{Kr}(^1S_0)$ separated atom limits, see the text.

orbit parameters for In and Tl, see Table VII, were used to couple the curves calculated for GaKr. The potential energy curves for InKr and TlKr obtained in this way are expected to be qualitatively correct; the curves are plotted in Figs. 6 and 7. As before, the plotted

DIPOLE TRANSITION MOMENTS CONNECTING THE LOW-LYING STATES OF TlKr WITH SPIN-ORBIT CORRECTIONS

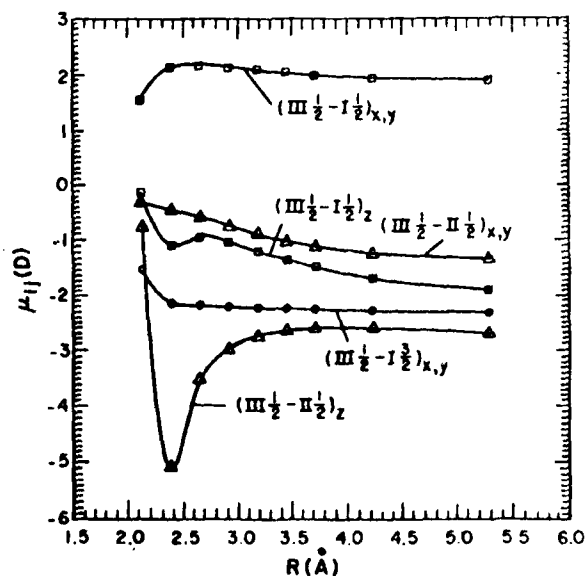


FIG. 8. Model dipole transition moments for the $\text{III } 1/2 - \text{I } 1/2$, $\text{III } 1/2 - \text{I } 3/2$, and $\text{III } 1/2 - \text{II } 1/2$ transitions in TlKr.

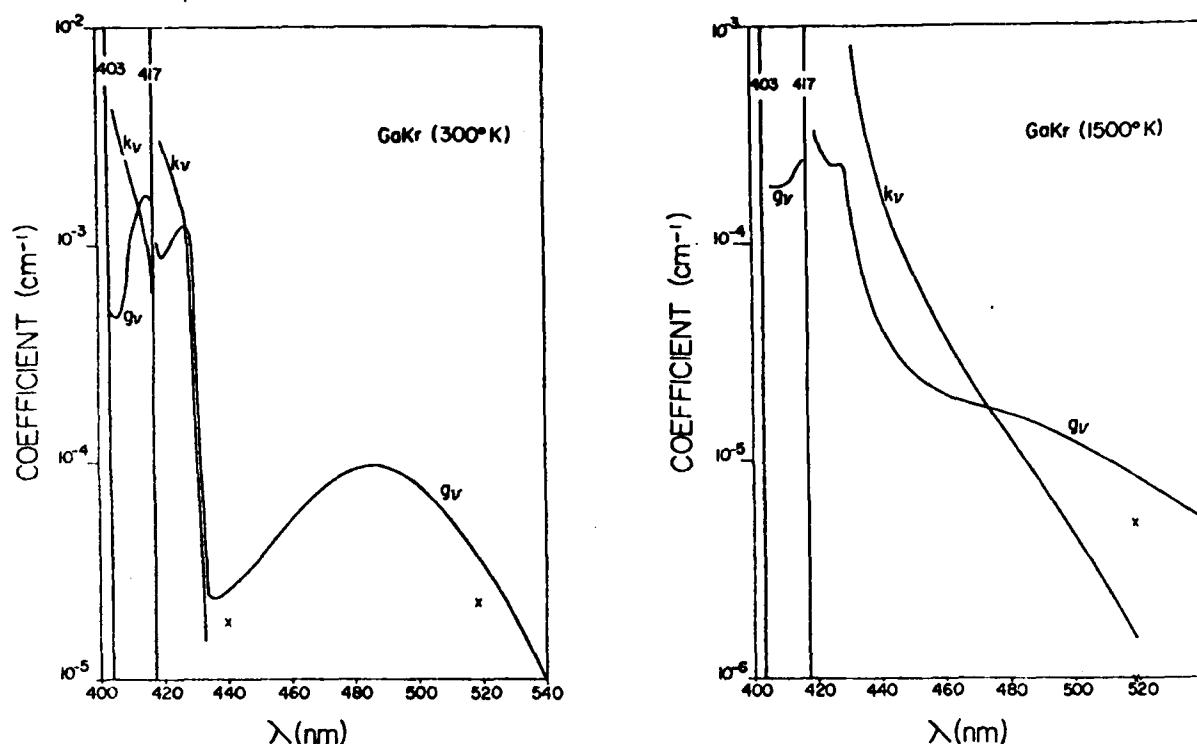


FIG. 9. Calculated absorption, $K_v(T)$, and stimulated emission, $g_v(T)$, coefficients for GaKr at $T = 300$ and 1500°K .

curves have been shifted to give the correct atomic excitation energies. The effect of the increasing spin-orbit interaction in the sequence $\text{Ga} < \text{In} < \text{Tl}$ is evident in Figs. 4, 6, and 7.

Using the transition moments obtained from the calculations on GaKr and the wavefunctions obtained from the TIKr simulation, the transition moments of TIKr have been estimated. The moments so obtained are plotted in Fig. 8.

VI. ABSORPTION AND STIMULATED EMISSION COEFFICIENTS FOR GaKr, InKr, AND TIKr

The interest in the Group IIIA-rare gas systems arises from the possibility of their use as visible laser systems. In order to judge their usefulness as lasers it is convenient to calculate the pure absorption, $K_v(T)$, and stimulated emission, $g_v(T)$, coefficients for the perturbed atomic transitions. Obtaining quantum mechanical results for these quantities would require a complex calculation which is not justified by the extrapolations used to obtain the InKr and TIKr curves. Consequently, we have used instead the method of Gallagher and co-workers,¹⁰ which is based on the classical Franck-Condon principle. In this approximation

$$g_v(T) = [M^*][X](\lambda^2/8\pi)A_0(J(\lambda/\lambda_0))I'_J(\nu T)$$

$$K_v(T) = [M][X](g^*/g)g_v(T) \exp[h(\nu - \nu_0)/kT]$$

and

$$I'_J(\nu, T) = 4\pi R(\nu)^2 \left(\frac{\nu}{\nu_0}\right)^4 \frac{1}{d\nu/dR(\nu)} \frac{D[R(\nu)]}{D(\infty)} \frac{g_m}{g_A} \times \exp\{-V^*[R(\nu)]/kT\}.$$

In these equations, J refers to the bands associated with the $^2S_{1/2} \rightarrow ^2P$ transition, ν_0 and λ_0 are the frequency and wavelength of the atomic transition with a transition rate of $A_0(J)$, $g^* = 2$ for the $^2S_{1/2}$ state and $g = 2J + 1$ for the 2P states, $D(R)$ is the transition dipole moment at R , g_m and g_A are the statistical weights of the excited molecular and parent atomic state, and $V^*(R)$ is the excited state potential curve relative to the energy of the excited atomic state. $[M]$, $[M^*]$, and $[X]$ are the concentrations of ground and excited metal atoms and of rare gas atoms at the temperature T .

In order to obtain $g_v(T)$ and $K_v(T)$, the calculated curves were first fit with cubic splines. The spline fit was then used to calculate $d\nu/dR$, and these quantities, along with the atomic transition rates,¹⁴ were used to calculate the absorption and stimulated emission coefficients for pressure and excitation conditions relevant to the experimental studies. We have calculated the coefficients for two different types of conditions. The high temperature results correspond to the case where the concentration of the metal is obtained from the vapor pressure of the metal itself, while the low temperature results correspond to obtaining the required concentration of the metal from vaporization of M_3 . This latter condition has been suggested by Gallagher² as a possible means of obtaining high concentrations of the metal at low temperatures. In both cases the densities used are

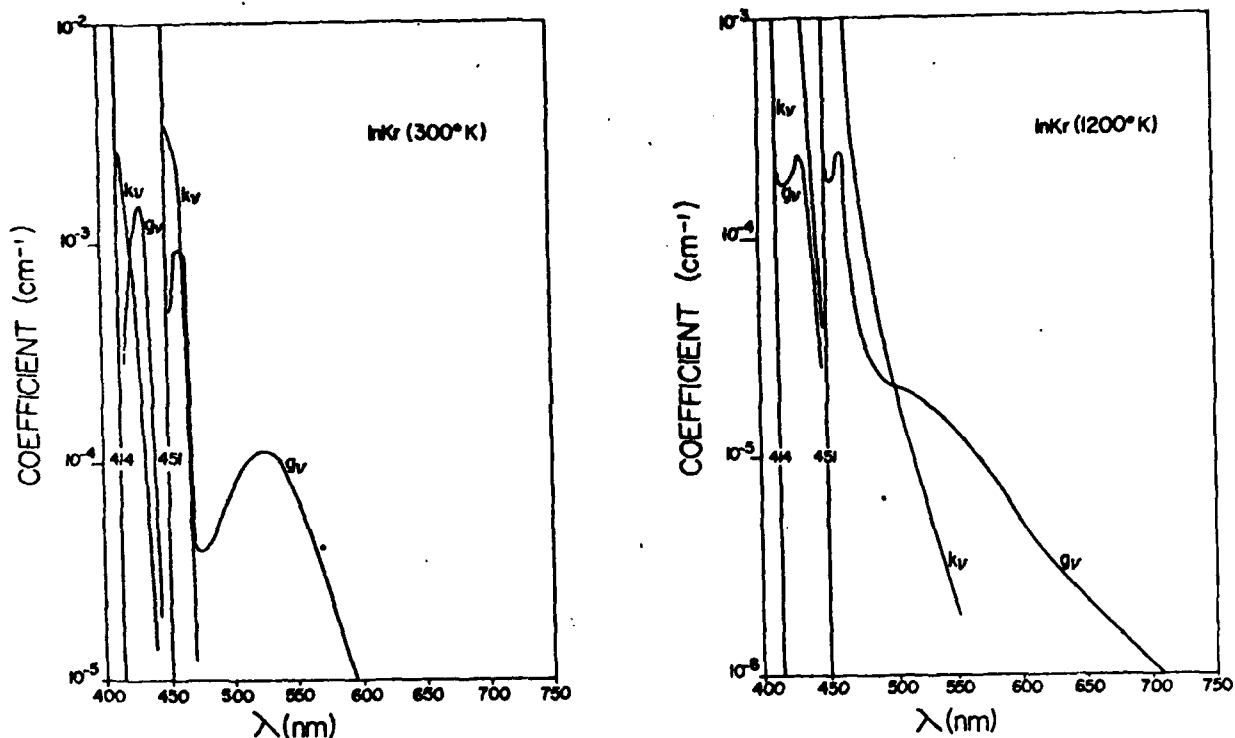


FIG. 10. Model absorption, $K_v(T)$, and stimulated emission, $g_v(T)$, coefficients for InKr at $T = 300$ and 1200°K .

$10^{20}/\text{cm}^3$ for [Kr], $10^{16}/\text{cm}^3 = 3[M(^2P_{1/2})] = 1.5[M(^2P_{3/2})]$, and $2 \times 10^{14}/\text{cm}^3$ for $[M(^2S_{1/2})]$. Since the blue wings of the $^2S_{1/2} - ^2P_{1/2,3/2}$ bands are due to transitions occurring at large R , where our curves are not expected to be

especially accurate, we have not calculated g_v and K_v in these regions.

The resulting absorption and stimulated emission coefficients for GaKr, InKr, and TlKr are given in Figs.

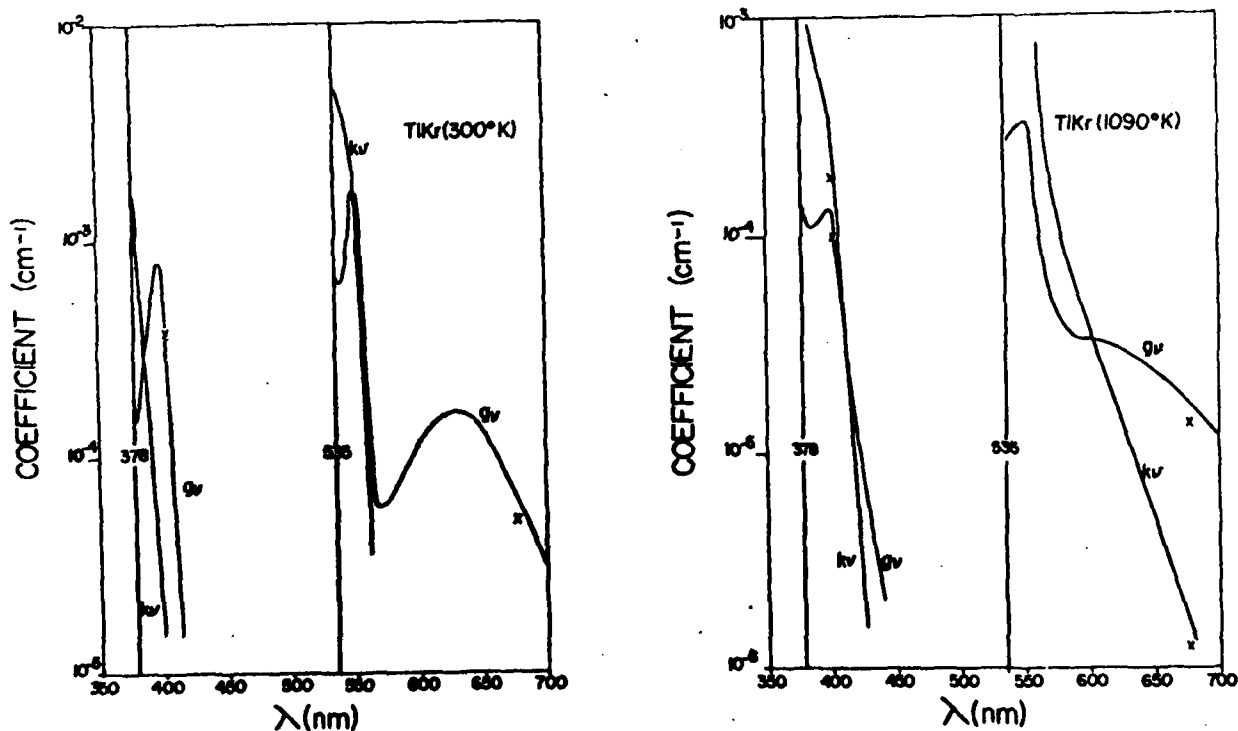


FIG. 11. Model absorption, $K_v(T)$, and stimulated emission, $g_v(T)$, coefficients for TlKr at $T = 300$ and 1090°K .

9-11. In these figures the solid lines are the total coefficients calculated by assuming that the transition moment, $D(R)$, is a constant. The X 's are the coefficients obtained by using the spatially averaged values of $D(R)$ calculated from Table VI and the appropriate spin-orbit parameters. For GaKr at 1500°K (Fig. 10) and for $403.4 < \lambda < 417.3$ nm, $K_v > 10^{-3}$ cm⁻¹. The dip in g_v close to the line center is due to the positive value of $V^*(R \sim 8a_0) - V^*(R = \infty)$.

The gain coefficient, which is approximately equal to $g_v - K_v$, can be estimated from these curves. For the frequencies at which gain occurs, the use of $D(R)$ decreases g_v , K_v , and the gain by 30-40% for GaKr and by 9-15% for TlKr. For TlKr the errors introduced by the extrapolation procedure are likely to be larger than those produced by using $D(\infty)$ rather than $D(R)$. The maximum gain occurs approximately at the minimum in the $III\ 1/2$ curve. Because g_v depends exponentially on V^* , changes in the well depth of the excited state would have a significant effect on g_v . If the well depth were larger for TlKr, as Gallagher and co-workers predict,¹ g_v and the gain would be larger. Likewise, since the excited state in TlXe is predicted¹ to be more bound than in TlKr, the gain should be larger for TlXe than for TlKr.

¹B. Cheron, R. Scheps, and A. Gallagher, J. Chem. Phys. **65**, 326 (1976).

²A. Gallagher, private communication.

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Chem. Phys. **65**, 2679 (1976).

⁴C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards, Circular No. 467, Vols. I-III. (U.S. GPO, Washington, D. C., 1949).

⁵T. H. Dunning, Jr., J. Chem. Phys. **66**, 1382 (1977).

⁶R. C. Raffanetti, J. Chem. Phys. **58**, 4452 (1973).

⁷T. H. Dunning, Jr. and P. J. Hay in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer, III (Plenum, New York, 1977), Chap. 1.

⁸T. H. Dunning, Jr. and P. J. Hay, J. Chem. Phys. **66**, 3767 (1977).

⁹W. J. Hunt and W. A. Goddard, III, Chem. Phys. Lett. **3**, 414 (1969).

¹⁰P. J. Hay and T. H. Dunning, Jr., J. Chem. Phys. **64**, 5077 (1976); T. H. Dunning, Jr., J. Chem. Phys. **65**, 3854 (1976). The POL-CI wavefunction is closely related to the first-order wavefunction of Schaefer, Harris, and co-workers, see, e.g., H. F. Schaefer, III, R. A. Klemm, and F. E. Harris, J. Chem. Phys. **51**, 4643 (1969).

¹¹The CI program cannot make full use of the atomic or diatomic symmetry. The numbers of configurations quoted in the text are for C_{2v} symmetry.

¹²For the states of interest here the generalized valence bond wavefunctions would also include the $s-p$ near-degeneracy configurations. As noted in the text these configurations are included in the POL-CI wavefunctions.

¹³P. J. Hay and T. H. Dunning, Jr., J. Chem. Phys. **66**, 1306 (1977).

¹⁴M. Norton and A. Gallagher, Phys. Rev. A **3**, 915 (1971).

¹⁵P. Bagus, Y. S. Lee, and K. S. Pitzer, Chem. Phys. Lett. **33**, 408 (1975).

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Appendix B

111

$$\begin{aligned} & \text{b}, \text{bx}) = 0; \\ & \text{b}, \text{by}) = 0; \\ & \text{b}, \text{bz}) = 0; \\ & (\text{a}/\text{c}) \cdot \text{a} \text{h}(\text{e}, \text{x}, \text{f}, \text{x}, \text{bx})/\text{r} \text{a}(\text{e}, \text{f}, \text{f}, \text{bb}); \\ & (\text{a}/\text{c}) \cdot \text{a} \text{h}(\text{e}, \text{y}, \text{f}, \text{y}, \text{by})/\text{r} \text{a}(\text{e}, \text{f}, \text{f}, \text{bb}); \\ & (\text{a}/\text{c}) \cdot \text{a} \text{h}(\text{e}, \text{z}, \text{f}, \text{z}, \text{bz})/\text{r} \text{a}(\text{e}, \text{f}, \text{f}, \text{bb}); \\ & (\text{b}/\text{c}) \cdot \text{a} \text{h}(\text{e}, \text{x}, \text{f}, \text{x}, \text{bx})/\text{r} \text{a}(\text{e}, \text{f}, \text{f}, \text{bb}); \\ & (\text{b}/\text{c}) \cdot \text{a} \text{h}(\text{e}, \text{y}, \text{f}, \text{y}, \text{by})/\text{r} \text{a}(\text{e}, \text{f}, \text{f}, \text{bb}); \\ & (\text{b}/\text{c}) \cdot \text{a} \text{h}(\text{e}, \text{z}, \text{f}, \text{z}, \text{bz})/\text{r} \text{a}(\text{e}, \text{f}, \text{f}, \text{bb}); \\ & -\text{a} \text{b}(\text{e}, \text{x}, \text{f}, \text{x}, \text{bx})/\text{r} \text{a}(\text{e}, \text{f}, \text{f}, \text{bb}); \\ & -\text{a} \text{b}(\text{e}, \text{y}, \text{f}, \text{y}, \text{by})/\text{r} \text{a}(\text{e}, \text{f}, \text{f}, \text{bb}); \\ & -\text{a} \text{b}(\text{e}, \text{z}, \text{f}, \text{z}, \text{bz})/\text{r} \text{a}(\text{e}, \text{f}, \text{f}, \text{bb}); \end{aligned}$$

[illegible]

```

da := sub(abx=0,aby=0,abz=0,rab=0,d3);
return fa;
end;
*****
q1 := (-3*cc*(ee,ff)+2/c);
q2 := (-3*cc*ra(cc,ff,bb)+7/d);
q3 := (-3*cc*ra(cc,ff,bb)+2);
q4 := (2*ra(cc,ff,bb)+2);
q5 := sinh(2*d*ra(cc,ff,bb));
q10 := 31*q2*q3*q4*q5;
q20 := (1*(OF(q1),H2)) / (4*cc+2)+q1 / (2*cc) - 11*q1*q4*r+2*q5 / 2;
let q20 := 120;
let cc := 1;
let q21 := q1 / (2*b);
let q22 := 1 / (2*b);
let q23 := 1 / (2*b);
let q24 := 1 / (2*b);
let q25 := 1 / (2*b);
let q26 := 1 / (2*b);
let q27 := 1 / (2*b);
comment *****
let r2(cc,ff) = ref,ra(cc,ff,bb) = ABX,AB(EY,FY,RY) = ABY,AB(EZ,FZ,RZ) = ABZ;
AH(EX,FX,RX) = AHX,AB(EX,FX,HX) = abx,d7(ey,fy,ry) = aby,dg(ez,fz,bz) = abz;
let r2(cc,ff,bb) = rab,d7(ex,fx,hx) = abx,d7(ey,fy,ry) = aby,dg(ez,fz,bz) = abz;
let d := c,rd:=c;
let q1 := 120;
let cc := 1;
let sinh(2*cc*ra(cc,ff,bb)) = sinh(z),cosh(2*cc*ra(cc,ff,bb)) = cosh(z);
q12 := sub(efx=0,efy=0,efz=0,ref=0,q11);
sub(sinh(z) = zz+zz**5/5+7*zz**5/12),cosh(z) = 1+zz**2/2+zz**4/24+zz**6/720,q12);
saveat q16;
sub(zz=2*cc*ra(cc,ff,bb),q16);
saveat q17;
q18 := sub(abx=0,aby=0,abz=0,rab=0,q17);
q28 := sub(efx=0,efy=0,efz=0,ref=0,q27);
q29 := ocant(q28);
q32 := sub(efx=0,efy=0,efz=0,ref=0,q31);
q33 := ocant(q32);
q35 := sub(efx=0,efy=0,efz=0,ref=0,q34);
q36 := ocant(q35);
q38 := sub(efx=0,efy=0,efz=0,ref=0,q37);
q39 := ocant(q38);
subt sat;
of nat;
factor rab;
out qn;
write "comment (s,s)";
q20 := 111;
q12 := 112;
q18 := 118;
write "comment (s,ox)";

```

! <HATIS>0020.31:10 WFF 15-NOV-74 9:55AM

```

q21 := q21;
write ("copy");
q24 := q24;
write ("copy");
q27 := q27;
q28 := q28;
write ("comment (px,xx)");
q31 := q31;
q32 := q32;
q33 := q33;
write ("comment (py,yy)");
q34 := q34;
q35 := q35;
q36 := q36;
write ("comment (pz,zz)");
q37 := q37;
q38 := q38;
q39 := q39;
write ("end");
quit;
on nat;

```

APPENDIX C

```

0001 SURROUTINE JKPOUT(P,DJ,CK,ISNX,IUNIT,HQ,DKO,CLOSED)
0002 IMPLICIT REAL*8(A-H,C-Z)
0003 LOGICAL CLOSEC
0004 DIMENSION H(1275),DJ(1275),DK(1275),HC(1),DKO(1)
0005 INTEGER*2 ISNX(50),IA,IB,IC,ID,IMU,IF
0006 COMMON/INTS/NINTS,IA(500),IB(500),IC(500),ID(500),
/ IMU(500),IF(500),V(500)

C WILL ADD 2J-K TC H
C IF CLOSED = FALSE, WILL ALSO ACC -K FOR OPEN SHELL TO HQ
C DJ AND CK ALWAYS CONTAIN TOTAL (CLOSED + OPEN) DENSITY
C MATRICES
C DKO CONTAINS "DK" DENSITY MATRIX FOR OPEN SHELL CREATALS
C ONLY
C TOTAL COULOMB + EXCHANGE INTERACTION IS
C TR(DB*H)+TR(DO*HO)
C READ(IUNIT)NINTS,IA,IB,IC,ID,IMU,IF,V
C IF(NINTS.EQ.0) GO TO 30
C DC 29 M=1,NINTS
C I=IA(M)
C J=IB(M)
C K=IC(M)
C L=ID(M)
C MU=IMU(M)
C VAL=V(M)
C GO TO (12,13,14,15,16,17,18,19,20,21,22,23,24,25),MU

12 H(II)=H(II)+VAL*(CJ(II)+CK(II))
H(II)=H(II)+VAL*(CJ(II)+CK(II))
IF(CLOSED) GO TO 29
HC(II)=HO(II)+VAL*DKC(II)
GO TO 29

13 IJ=ISNX(I)+J
II=ISNX(I)+I
JJ=ISNX(J)+J
H(IJ)=H(IJ)+VAL*(CJ(IJ)+DJ(IJ)+DK(IJ))
H(II)=H(II)+VAL*DK(JJ)
H(JJ)=H(JJ)+VAL*DK(II)
IF(CLOSED) GC TC 29
H(IJ)=HO(IJ)+VAL*DKO(IJ)
H(II)=HO(II)+VAL*DKO(JJ)
H(JJ)=HC(JJ)+VAL*DKC(II)
GO TO 29

14 II=ISNX(I)+I
KK=ISNX(K)+K
IK=ISNX(I)+K
H(II)=H(II)+VAL*DJ(KK)
H(KK)=H(KK)+VAL*DJ(II)
H(IK)=H(IK)+CK(IK)*VAL
IF(CLOSED) GC TO 29
H(IK)=HO(IK)+VAL*DKO(IK)
GC TO 29

15 IL=ISNX(I)+L
II=ISNX(I)+I
H(IL)=H(IL)+VAL*(CJ(II)+CK(II))
H(II)=H(II)+VAL*(CJ(IL)+DK(IL))
IF(CLOSED) GO TO 29
H(IL)=HC(IL)+VAL*DKC(II)
H(II)=HO(II)+VAL*DKO(IL)*2.D0
GC TO 29

```

```

0050      KL=ISNX(K)+L
0051      IL=ISNX(I)+I
0052      IL=ISNX(I)+L
0053      IK=ISNX(I)+K
0054      H(KL)=H(KL)+(VAL+VAL)*DJ(IJ)
0055      H(IL)=H(IL)+(VAL+VAL)*DJ(KL)
0056      H(IL)=H(IL)+VAL*DK(IK)
0057      H(IK)=H(IK)+VAL*DK(IL)
0058      IF(CLOSED) GO TO 29
0059      HO(IL)=HO(IL)+VAL*DKC(IK)
0060      HO(IK)=HO(IK)+VAL*DKO(IL)
0061      GC TO 29
0062      JJ=ISNX(J)+J
0063      IJ=ISNX(I)+J
0064      H(JJ)=H(JJ)+(VAL+VAL)*(CJ(IJ)+CK(IJ))
0065      H(IJ)=H(IJ)+VAL*(DJ(JJ)+DK(JJ))
0066      IF(CLOSED) GO TO 29
0067      HO(JJ)=HO(JJ)+VAL*DKC(IJ)*2.00
0068      HO(IJ)=HO(IJ)+VAL*DKO(JJ)
0069      GC TO 29
0070      JK=ISNX(J)+K
0071      GO TO 27
0072      JK=ISNX(K)+J
0073      KK=ISNX(K)+K
0074      IJ=ISNX(I)+J
0075      IK=ISNX(I)+K
0076      H(KK)=H(KK)+(VAL+VAL)*DJ(IJ)
0077      H(IJ)=H(IJ)+VAL*DJ(KK)
0078      H(JK)=H(JK)+VAL*DK(IK)
0079      H(IK)=H(IK)+VAL*DK(JK)
0080      IF(CLOSED) GC TO 29
0081      HO(JK)=HO(JK)+VAL*DKO(IK)
0082      HO(IK)=HO(IK)+VAL*DKC(JK)
0083      GO TO 29
0084      IJ=ISNX(I)+J
0085      JL=ISNX(J)+L
0086      JJ=ISNX(J)+J
0087      IL=ISNX(I)+L
0088      H(JL)=H(JL)+VAL*(DJ(IJ)+CJ(IJ)+CK(IJ))
0089      H(IJ)=H(IJ)+VAL*(DJ(JL)+DJ(JL)+DK(JL))
0090      H(JJ)=H(JJ)+(VAL+VAL)*DK(IL)
0091      H(IL)=H(IL)+VAL*DK(JJ)
0092      IF(CLOSED) GO TO 29
0093      HC(JL)=HO(JL)+VAL*DKC(IJ)
0094      HO(IJ)=HO(IJ)+VAL*DKO(JL)
0095      HO(JJ)=HO(JJ)+VAL*DKC(IL)*2.00
0096      HO(IL)=HO(IL)+VAL*DKO(JJ)
0097      GO TO 29
0098      IL=ISNX(I)+L
0099      IJ=ISNX(I)+J
0100      II=ISNX(I)+I
0101      JL=ISNX(J)+L
0102      H(IL)=H(IL)+VAL*(DJ(IJ)+DJ(IJ)+DK(IJ))
0103      H(IJ)=H(IJ)+VAL*(CJ(IL)+DJ(IL)+DK(IL))
0104      H(II)=H(II)+(VAL+VAL)*DK(JL)
0105      H(JL)=H(JL)+VAL*DK(II)
0106      IF(CLOSED) GC TO 29
0107      HO(IL)=HO(IL)+VAL*DKO(IJ)
0108      HO(IJ)=HO(IJ)+VAL*DKO(IL)

```

```

0109      PC(I1)=PC(I1)+VAL*DKO(JL)*2.D0
0110      HC(JL)=HC(JL)+VAL*DKC(I1)
0111      GO TO 29
0112      IJ=ISNX(I)+J
0113      KJ=ISNX(K)+J
0114      JJ=ISNX(J)+J
0115      IK=ISNX(I)+K
0116      H(KJ)=H(KJ)+VAL*(CJ(IJ)+CJ(IJ)+DK(IJ))
0117      H(IJ)=H(IJ)+VAL*(CJ(KJ)+DJ(KJ)+DK(KJ))
0118      H(JJ)=H(JJ)+(VAL+VAL)*DK(IK)
0119      H(IK)=H(IK)+VAL*DK(JJ)
0120      IF(CLCSED) GO TO 29
0121      HQ(KJ)=HQ(KJ)+VAL*DKC(IJ)
0122      HQ(IJ)=HQ(IJ)+VAL*DKO(KJ)
0123      HC(JJ)=HC(JJ)+VAL*DKC(IK)*2.D0
0124      HQ(IK)=HQ(IK)+VAL*DKC(JJ)
0125      GC TO 29
0126      JL=ISNX(J)+L
0127      JK=ISNX(J)+K
0128      GC TO 26
0129      JL=ISNX(J)+L
0130      JK=ISNX(K)+J
0131      GC TO 26
0132      JL=ISNX(L)+J
0133      JK=ISNX(K)+J
0134      KL=ISNX(K)+L
0135      IJ=ISNX(I)+J
0136      IL=ISNX(I)+L
0137      IK=ISNX(I)+K
0138      H(JL)=H(JL)+VAL*DK(IK)
0139      H(IK)=H(IK)+VAL*DK(JL)
0140      H(IL)=H(IL)+VAL*DK(JK)
0141      H(JK)=H(JK)+VAL*DK(IL)
0142      IF(CLCSED) GC TO 290
0143      HO(JL)=HO(JL)+VAL*DKC(IK)
0144      HO(IK)=HO(IK)+VAL*DKC(JL)
0145      HO(IL)=HO(IL)+VAL*DKC(JK)
0146      HO(JK)=HO(JK)+VAL*DKO(IL)
0147      VAL=VAL+VAL
0148      H(KL)=H(KL)+VAL*DJ(IJ)
0149      H(IJ)=H(IJ)+VAL*DJ(KL)
0150      CCNTINUE
0151      IF(LAST.EQ.0) GO TO 11
0152      RETURN
0153      END

```



```

0001 REAL FUNCTION QINT*(K)
0002 IMPLICIT REAL*(A-H,O-Z)
0003 EXTERNAL DS1,DS2,DS3,CS4,CS5,CS6,CS7,CS8,CS9
0004 LOGICAL INTG
0005 COMMON/INT/C,CK,EAB,DKG,IITYPE
0006 COMMON/SCLR/EXI,EXJ,IITYPE,JTYPE,ICNTR,JC,NTR,M,CUT,CUT2,CUT3,
0007 U,ALPHA,ALPHAQ,AP(4)
0008 CCMGCM/FACT/FACTCK(15),IPCT
0009 DATA SQ3/1.73205080756887D0/
0010 DATA FI/3.14159265358979D0/
0011 DATA NAPP,STEPM/4.200C,C0/
0012 DATA EPR/1.D-16/
0013 DATA NGC/6/
0014 C***** WARNING INTERVALS FOR G032 DECREASED*****
0015 C***** INCREASED INTEGRATION PARAM
0016 C***** PROGRAM USES INTEGRAL EXPRESSIONS OBTAINED FROM REDUCE
0017 C IITYPE=1,S
0018 C 2,FX
0019 C 3,PY
0020 C 4,PZ,Z ASSUMED ALONG DIRECTION OF BOND
0021 ICNTR=1, FOR A THE CLOSED SHELL ATOM ON WHICH EFFECTIVE POTENTIAL
0022 IS CENTERED
0023 2 FOR ATOM B, NGN-CLOSED SHELL
0024 C WARNING 01 AND 04 CODE DOES NOT CONTAIN EFX,EFY ETC TERMS
0025 C WHICH WOULD BE NEEDED FOR MOLECULES
0026 IF(ICNTR.EQ.0) GO TO 100
0027 DK=CUT2
0028 DKQ=CUT3
0029 GO TO 99
0030 DK=CUT
0031 QINT=0.0D0
0032 IF(IITYPE.LE.4.AND.JTYPE.LE.4.OR.K.GT.8.OR.K.LE.0) GO TO 101
0033 WRITE(6,600) IITYPE,JTYPE,K
0034 600 FORMAT(1H,25P*****ERRRCF***** /
0035 U 1H,24PONLY TYPE,LE,4 ALLOWED /
0036 U 1H,24HK=,IS,5X,16HK MUST BE 1 TO 8 /
0037 1 1H,20H***** /
0038 RETURN
0039 IJTYPE=IITYPE+JTYPE
0040 ICNTR=ICNTR+JCNTNTR
0041 GC TO (111,112,113,111,112,113,111,112,113,117,118),K
0042 IF((IITYPE.NE.1.OR.JTYPE.NE.4).AND.(JTYPE.NE.1.OR.IITYPE.NE.4))
0043 U .AND.(IITYPE.NE.JTYPE)) GO TO 115
0044 IF(K.F2.1.AND.((IITYPE.EQ.2.CR.IJTYPE.EQ.8).AND.IJCNTNTR.EQ.2)
0045 U .OR.((IITYPE.EQ.4.OR.IJTYPE.EQ.6).AND.IJCNTNTR.EQ.2))) GO TO 115
0046 IF(K.EQ.4.AND.((IITYPE.EQ.1.OR.JTYPE.EQ.1).AND.IJCNTNTR.EQ.2)) GO TO 115
0047 GO TO 120
0048 IF((IITYPE.NE.2.OR.(IITYPE.NE.1.AND.IITYPE.NE.4))
0049 U .AND.(IITYPE.NE.2.OR.(JTYPE.NE.1.AND.JTYPE.NE.4))) GO TO 115
0050 IF(K.EQ.2.AND.(IITYPE.EQ.4.OR.JTYPE.EQ.4).AND.IJCNTNTR.EQ.2)
0051 U GO TO 115
0052 IF(K.EQ.5.AND.(IITYPE.EQ.1.OR.JTYPE.EQ.1).AND.IJCNTNTR.EQ.2)
0053 U GO TO 115
0054 GO TO 120
0055 IF((IITYPE.NE.3.OR.(IITYPE.NE.1.AND.IITYPE.NE.4))
0056 U .AND.(IITYPE.NE.3.CR.(IITYPE.NE.1.AND.JTYPE.NE.4))) GO TO 115
0057 IF(K.EQ.3.AND.(IITYPE.EQ.4.OR.JTYPE.EQ.4).AND.IJCNTNTR.EQ.2)
0058 U GO TO 115

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```

0036 IF(K.EQ.6.AND.(ITYPE.EQ.1.OR.JTYPE.EQ.1).AND.IJCNTN.EQ.2)
      U GO TC 115
0037 GO TO 120
0038 IF((ITYPE.NE.JTYPE).OR.(ITYPE.NE.2.AND.IJTYPE.NE.3)) GO TO 115
0039 GO TO 120
0040 IF((ITYPE.NE.2.OR.JTYPE.NE.3)
      U .AND.(ITYPE.NE.3.OR.JTYPE.NE.2)) GO TO 115
      GO TO 120
0041 RETURN
0042 C=EXI+EXJ
0043 HM3=0.000
0044 FVA=0.000
0045 HM5=0.000
0046 FXD0=1.00
0047 IF(ICNTR.EQ.JCNTR) GC TC 130
0048 EXPREF=EXP(-EXI*EXJ**2/C)
0049 IF(EXPREF.EQ.0.000) RETURN
0050 IF(ICNTR.EQ.1) GC TC 125
0051 RAD=EXI**R/C
      GC TC 130
0052 RAD=EXJ**R/C
      GC TC 130
0053 RAD=EXJ**R/C
      GC TC 130
0054 EXPREF=1.00
0055 IF(ICNTR.EQ.1) GO TO 135
0056 RAD=EXI**R/C
      GC TC 130
0057 RAD=EXJ**R/C
      GC TC 130
0058 EXPREF=1.00
0059 IF(ICNTR.EQ.1) GO TO 135
0060 RAD=EXI**R/C
      GC TC 130
0061 RAD=EXJ**R/C
      GC TC 130
0062 EXP5=1.00
0063 C2=C*C
0064 C3=C2*C
0065 RAD2=RAB*RAB
0066 PAR3=RAB2*RAB
0067 IF(IJTYPE.EQ.2) GC TC 190
0068 AEX=0.000
0069 ABY=0.000
0070 ABZ=RAB
0071 FFX=0.000
0072 EFY=0.000
0073 EFZ=0.000
0074 IF(ICNTR.NE.JCNTR) EFZ=R
0075 RAD4=RAB2*RAB2
0076 RAD5=RAB2*RAB2
0077 RAD6=RAB3*RAB3
0078 RAD7=RAB3*RAB4
0079 C4=C2*C2
0080 ABX2=C.000
0081 ABY2=0.000
0082 ABZ2=ABZ*ABZ
0083 ADZ3=ADZ*ADZ
0084 IF(ITYPE.NE.1) A=EXJ
0085 IF(JTYPE.NE.1) A=EXI
0086 IF(ITYPE.EQ.1.OR.JTYPE.EQ.1) GC TC 190
      C DEFINITION AF A AND B IMPORTANT IF EXX,REY.NE./
0087 IF(ICNTR.NE.2) GC TO 188
      A=EXI
      B=EXJ
      GO TO 199
0088 A=EXJ
0089
0090
0091
0092
0093
0094
0095
0096
0097
0098
0099
0100
0101

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0002      R=EXI
0003      C5=C4*0
0004      RAB2=PARB1*PARB4
0005      RAB2=PARB3*PARB
0006      ABX3=0.000
0007      ABY3=0.000
0008      ABX4=0.000
0009      ABY4=0.000
0010      AB74=ABZ2*ABZ2
0011      EFZ2=C.000
0012      EFY2=0.000
0013      EFZ2=EFZ*FFZ
0014      GO TO 191
0015      IF (ICNTR+ITYPE.EQ.2.OR.JCNTR+JTYPE.EQ.2) EFZ=-EFZ
0016      IF (ICNTR+ITYPE.EQ.2) EFZ=-EFZ
0017      REXP=DSQR((-DLCG(1.D-16)/C)
0018      C**RETTTER INT LIMITS*****
0019      PMIN=CMAX1(RAE-REXP,0.000)
0020      RMAX=PARB*REXP
0021      HEXP=REXP*2.**(NAPF-1)
0022      HIN=HEXP*2.**(NAPF-1)
0023      INTC=(C.LE..100.AND.RAB.LE.10.000).CR.
0024      U (C.GE.1.D-10.AND.RAB.LT.100)
0025      IF (K.GE.4) GO TO 400
0026      IF (INTC) GO TO 195
0027      C*****WARNING: ALL INTEGRALS DONE BY GAUSSIAN QUAD*****
0028      C** REMOVE C FOR ITROMB
0029      C*****WARNING: GAUSSIAN QUAD CHANGED TO 4 INTERVALS
0030      CALL NDCG32(RMIN,FMX,DS1,HM1,NGQ)
0031      IF (RAB.GE.1.D-10) CALL NDCG32(RMIN,FMX,DS2,HM2,NGQ)
0032      GO TO 199
0033      195 CALL ITROMB(DS1,HIN,ERR,NAPP,FM1,IERR,RMIN)
0034      IF (RAE.GE.1.D-10)
0035      .CALL ITROMB(DS2,HIN,ERR,NAPP,HM2,IERR,RMIN)
0036      CONTINUE
0037      601 FCRMAT(1H,4FM1=E27.16,5X,4HFM2=E27.16)
0038      608 FCRMAT(1H,5HMIN=E15.6,5X,5HMAX=E15.6)
0039      IF (JTYPE.NE.2) GO TO 200
0040      C
0041      QINT=PI*(2.*HM2/(C*RAE)-HM1/(C2*PARB2))/EXP0
0042      QINT=QINT*EXPREF
0043      RETURN
0044      CONTINUE
0045      IF (ITYPE.EQ.1.OR.JTYPE.EQ.1).AND.K.NE.1) GO TO 205
0046      IF (INTC) GO TO 204
0047      IF (RAB.GE.1.D-10) CALL NDCG32(RMIN,FMX,DS3,HM3,NGQ)
0048      GO TO 205
0049      204 IF (RAB.GE.1.D-10)
0050      .CALL ITROMB(DS3,HIN,ERR,NAPP,HM3,IERR,RMIN)
0051      CONTINUE
0052      602 FCRMAT(1H,4HFM3=E27.16)
0053      IF (ITYPE.NE.1.AND.JTYPE.NE.1) GO TO 300
0054      GO TO (201,202,203),K
0055      C
0056      < S / Q1 / P2 >
0057      201 IF (RAB.LT.1.D-10) GO TO 211
0058      Q1= (-PI*(6*PARB*HM2*ABZ2*C-2*HM2*PARB3*(2*ABZ*EFZ*C*A-(2*C2*
0059      .ABZ2-C))+(2*ABZ*HM1*PARB2*EFZ*A-(HM1*(PARB2*(2*ABZ2*C-1)+3*PARB2)
0060      .+4*PARB2*C2*HM3*ABZ2)))/(2*EXP0*EXP5*C3*PARB5)
0061      CINT=Q1*EXPREF
0062      RETURN

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GINT

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0139      GINT=4.*PI*HM1/3.
0140      RETURN
0141      IF(RAF.LT.1.D-10) GO TO 212
0142      C U2= < S / Q2 / PX >
0143      Q2= ((2*C*PAB2*ABX2-RAB2+3*ABX2)-2*ABX*EFX*A*RAB2)*HM1+2*((C
0144      -2*C2*ABX2)*RAB3-3*RAB2+3*ABX2+2*ABX*EFX*C*A*RAB3)*HM2+4*HM3*
0145      C2*ABX2*ABX2)*PI)/(2*E*PC*E*PF5*C3*RAB5)
0146      GINT=C2*EXPREF
0147      RETURN
0148      GINT=4.*PI*HM1/3.
0149      RETURN
0150      IF(RAB.LT.1.D-10) GO TO 213
0151      C Q3= < S / Q3 / PY >
0152      Q3= ((2*ABY2*C-1)*RAB2+3*ABY2)*HM1-2*((2*C2*ABY2-C)*HM2*RAB3+4*
0153      HM3*C2*RAB2*ABY2)*EXP5M)/(2*C3*RAB5)*EXPREF
0154      GINT=C3
0155      RETURN
0156      GINT=4.*PI*HM1/3.
0157      RETURN
0158      CONTINUE
0159      IF(IJTYPE.NE.8) GO TO 302
0160      IF(INIC) GO TO 301
0161      IF(RAB.GE.1.D-10) CALL NDCG32(RMIN,RMAX,DS4,HM4,NGQ)
0162      GO TO 302
0163      IF(RAB.GE.1.D-10)
0164      /CALL ITDGM(RDS4,HIN,FFR ,NAPP,HM4,IERR,RMIN)
0165      CONTINUE
0166      FCRMAT(1H,4HMM4=F27.16)
0167      GO TO (310,320,330),K
0168      GO TO (310,312,313,314),I TYPE
0169      C < PX(E) / Q1(F) / PY(E) >
0170      Q1= (-ABZ*PI*(6*HM2*RAB3*C-(3*HM1*RAB2+4*C2*HM3*RAB4)))/(4*
0171      EXP0*EXP5*RAE7*C4)
0172      GINT=C1*EXPREF
0173      RETURN
0174      C < PY(E) / Q1(F) / PY(E) >
0175      Q1= (-ABZ*PI*(6*HM2*RAB3*C-(3*HM1*RAB2+4*C2*HM3*RAB4)))/(4*
0176      EXP0*EXP5*RAE7*C4)
0177      GINT=C1*EXPREF
0178      RETURN
0179      C < PZ / Q1 / PZ >
0180      Q1= (PI*(30*RAB*HM2*AEZ3+C-2*HM2*(ABZ*(9*RAB3*C+4*C2*RAB5+4*
0181      RAB5*RAE22*C*A)-2*(3*RAB3*(2*C2*APZ3+ABZ2*EFZ*(B-A)*C)+2*C2*
0182      RAB5*ABZ2*EFZ*(B-A)+2*C3*RAE5*AEZ3-HAB5*EFZ*(B-A)*C))+ABZ*(
0183      HM1*(9*RAE92+4*RAB4*(B*EFZ2*A+C))+12*C2*HM3*RAB4)-(HM1*(6*RAB2
0184      *(ABZ2*EFZ*(B-A)+2*AEZ3*(C)+4*C2*RAE4*ABZ3+4*ABZ2*EFZ*RAB4*(B-
0185      A)*C-2*EFZ*RAB4*(B-A)+15*ABZ3)+24*RAE2*C2*HM3*ABZ3-8*RAB3*C3*
0186      HM4*ABZ1+8*C2*HM3*ABZ2*EFZ*RAB4*(B-A)+16*HM3*C3*RAB4*ABZ3)))/
0187      (4*EXP0*EXP5*RAE7*C4)
0188      GINT=Q1*EXPREF
0189      RETURN
0190      C < PX / Q2 / PZ >
0191      Q2= IF(I TYPE.EQ.2) GO TO 321
0192      A=EXI
0193      B=EXJ
0194      IF(ICNTR.EQ.1) EFZ=-R
0195      GC TO 322
0196      Q=EXI
0197      321

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0176 A=EXJ
0177 IF(JCNTR.EQ.1) EFZ=-R
0178 Q2= (-PI*(2*8*(HM1*(2*C*RAB4*AE2+3*RAB2*ABX2-RAB4)-2*ABX*EFX
322 . *RAB4)-2*HM2*((3*RAB3*ABX2-RAB5)*C+2*C2*RAB5*ABX2)-2*ABX*
. EFX*C2*RAB5)+4*HM3*C2*RAE4*ABX2)*EFZ+HM1*ABZ*((2*(6*RAB2*
. ABX2-RAB4)*C+4*C2*RAE4*AE2-3*RAB2+15*ABX2)-2*(2*C*RAB4+3*
. RAB2)*ABX*EFX+4)-2*HM2*ABZ*((2*(6*RAB3*ABX2-RAB5)*C2-3*C*RAB3
. +4*C3*RAB5*ABX2)-2*(3*C*RAE3+2*C2*RAE5)*ABX*EFX+4+15*RAB3*
. ABX2)+4*HM3*ABZ*((6*RAB2*ABX2-RAB4)*C2+4*C3*RAE4*ABX2)-2*ABX
. *EFX*4*C2*RAB4)-8*HM4*ABZ*C3*RAB3*ABX2))/((4*EXP0*E*XP5*RAB7*C4
. )
0179 QINT=Q2*EXPREF
0180 RETURN
C < PY / Q3 / P2 >
330 IF(ITYPE.EQ.3) GO TO 331
A=FXJ
R=EXI
0181 IF(JCNTR.EQ.1) EFZ=-R
0182 GO TO 332
331 A=EXI
R=EXJ
0183 IF(ICNTR.EQ.1) EFZ=-R
0184 Q3= (PI*EXP54*((30*RAB1*AB7*HM2*ABY2*C+2*ABY*AB*EFY*(2*EFZ*(HM1*
. RAB4-2*HM2*RAB5*C)+A-AE2*(3*HM1*RAB2+2*HM1*RAB4*C-4*HM2*C2*
. RAB5-6*HM2*RAB3*C+4*HM3*C2*RAB4))+ (2*EFZ*(HM1*(2*ABY2*C-1))*
. RAB4+3*RAB2*ABY2)-2*HM2*(2*C2*RAB5*ABY2+3*RAB3*ABY2*C-RAB5*C)
. +4*HM3*C2*RAB4*ABY2)-2*HM2*(A-AE2*(4*HM1*C2*RAE4*ABY2+12*HM1*RAE2*
. ABY2*C-3*HM1*RAB2-2*HM1*RAB4*C+15*HM1*ABY2-24*HM2*C2*RAB3*
. ABY2+4*HM2*C2*RAE5-8*HM2*C3*RAB5*ABY2+6*HM2*RAB3*C+24*HM3*C2*
. RAB2*ABY2-4*HM3*C2*RAB4+16*HM3*C3*RAE4*ABY2-8*HM4*C3*RAB3*
. ABY2)))/(4*C4*EXP0*RAE7)
0185 QINT=Q3*EXPREF
0186 RETURN
400 CCNTINUE
C
0190 IF(IMTC) GO TO 401
0191 CALL NDGG32(RMIN,RMAX,DS5,HM1,NGQ)
0192 IF(RAB.LT.1.D-10) GC TC 449
0193 CALL NDGG32(RMIN,RMAX,DS6,HM2,NGG)
0194 CALL NDGG32(RMIN,RMAX,DS7,HM3,NGQ)
0195 GC TO 449
0196 CALL ITROMB(DS5,HIN,ERR,NAPP,HM1,IERR,RMIN)
0197 IF(RAB.LT.1.D-10) GC TO 449
0198 CALL ITROMB(DS6,HIN,ERR,NAPP,HM2,IERR,RMIN)
0199 CALL ITROMB(DS7,HIN,ERR,NAPP,HM3,IERR,RMIN)
0200 CCNTINUE
0201 FORMAT(IH,4HHM2=E27.16,EX,4HHM2=E27.16,5X,4HHM3=E27.16)
0202 IF(ITYPE.NE.2) GC TC 450
0203 C < S / 24 / S >
0204 QINT=PI*(2*HM3+3*HM1/(2*C2*RAB2)-3*HM2/(C*RAB))/(C*RAB*EXP0)
0205 QINT=QINT*EXPREF
0206 RETURN
450 CONTINUE
C
0207 IF(ITYPE.EQ.1,OR,JTYPE.EG.1).AND.K.NE.4).OR.K.EQ.7) GO TO 452
0208 IF(INTC) GO TO 451
0209 IF(RAB.GE.1.D-10) CALL NDGG32(RMIN,RMAX,DS8,HM4,NGQ)
0210 GO TO 452
0211 IF(RAB.GE.1.D-10)
0212 /CALL ITROMB(DS8,HIN,ERR,NAPP,HM4,IERR,RMIN)
0213 CONTINUE

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QINT

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0247 *PAB5*(4*C3*ABZ4-6*EFZ*ABZ*(B-A)*C+3*C)+4*AB7*8*C*A*EFZ2))+2
0248 *ABZ2*((135*HM1*AB2+18*HM1*AB4*B*A*EFZ2+54*HM1*AB4*AB2*HM1*
0249 C2*AB6+222*AB4*C2*HM3+24*C2*HM3*AB6*8*AB6*8*AB6*8*AB6*8*AB6*8*
0250 HM4+20*HM3*AB6*C3+8*HM3*4*AB6*8*AB6*8*AB6*8*AB6*8*AB6*8*AB6*8*
0251 )-(13*HM1*(30*AB2*(AB7*3*EFZ*(B-A)+2*C*ABZ4)+3*AB4*(4*C2*ABZ4
0252 +4*ABZ3*EFZ*(B-A)*C-6*EF7*ABZ*(B-A)+3)-4*AB6*(EFZ*ABZ*(B-A)*
0253 C-R*A*EFZ2)+105*AB74)+54*C*AB2*C2*HM3*ABZ4+48*AB4*(3*C2*HM3*
0254 ABZ3*EF7*(B-A)+6*HM3*3*ABZ4+C4*HM5*ABZ4)-8*C2*HM3*(5*AB6*(2
0255 *EFZ*ABZ*(B-A)-1)-2*AB6*EFZ2)-240*AB3*3*HM4*ABZ4-48*
0256 RAB5*HM4*(C3*ABZ3*EFZ*(B-A)+2*C4*ABZ4)+16*HM3*(3*AB6*(C3*
0257 ABZ3*EFZ*(B-A)+C4*AEZ4)-(3*EFZ*ABZ*AB8*(B-A))+8*C3*HM4*AB7*
0258 (2*EFZ*ABZ*(B-A)-1)))/(16*EXP5*EXP0*C5*AB9)
0259 GINT=G4*EXPREF
0260 RETURN
0261 QINT=8.*PI*HM1/15.
0262 RETURN
0263 C < PX / Q5 / PZ >
0264 550 IF(RAB*LT.1.D-10) GO TO 551
0265 IF(ITYPE.EQ.2) GC TO 553
0266 P=EXJ
0267 IF(ICNTR.EQ.1) EFZ=-R
0268 GO TO 552
0269 R=EXI
0270 A=EXJ
0271 IF(JCNTR.EQ.1) EFZ=-R
0272 Q5= (-0.1*(ABZ2*(210*AB2*HM2*C*ABX2+(2*ABX*EFX*(8*AB6*HM3*C3+6
0273 *HM1*C*AB4+15*HM1*AB2-30*HM2*C*AB3-12*HM2*C2*AB5+24*HM3*
0274 C2*AB4-8*HM4*C3*AB5)*A+8*AB6*HM3*(C3-2*C4*ABX2)-3*HM1*(2*(
0275 10*AB2*ABX2-RAB4)*C+4*C2*AB4*ABX2-5*AB2+35*ABX2)+6*HM2*(2*
0276 (10*AB3*ABX2-RAB5)*C2-5*C*AB3+4*C3*AB5*ABX2)-12*HM3*(15*
0277 RAB2*ABX2-2*AB4)*C2+8*C3*AB4*ABX2)+8*HM4*(10*AB3*ABX2-
0278 RAB5)*C3+4*C4*AB6*HM3*ABX2)-16*HM5*C4*AB4*ABX2))+2*ABZ*B*EFZ*(2
0279 *ABX*EFX*(4*AB6*HM3*ABX2+3*(HM1*AB4-2*HM2*C*AB5))*A+(4*AB6*
0280 HM3*(C2-2*C3*ABX2)-(3*HM1*(2*C*AB4*ABX2+5*AB2*ABX2-RAB4))-6*
0281 HM2*(5*AB3*ABX2-RAB5)*C+2*C2*AB5*ABX2)+24*HM3*C2*AB4*ABX2
0282 -8*HM4*C3*AB5*ABX2))-(2*ABX*EFX*(4*AB6*HM3*ABX2+3*HM1*AB4-6
0283 *HM2*C*AB5)*A+4*AB6*HM3*(C2-2*C3*ABX2)-3*HM1*(2*C*AB4*ABX2
0284 +5*AB2*ABX2-RAB4))+6*HM2*(5*AB3*ABX2-RAB5)*C+2*C2*AB5*ABX2
0285 )-24*HM3*C2*AB4*ABX2+8*HM4*C3*AB5*ABX2)))/(8*EXP0*EXP5*C5*
0286 RAB9)
0287 QINT=G5*EXPREF*SC3
0288 RETURN
0289 551 GINT=4.*PI*HM1/15.*S03
0290 RETURN
0291 C < PY / Q6 / PZ >
0292 560 IF(RAB*LT.1.D-10) GO TO 551
0293 IF(ITYPE.EQ.3) GC TO 561
0294 A=EXJ
0295 B=EXI
0296 IF(JCNTR.EQ.1) EFZ=-R
0297 GC TO 562
0298 A=EXI
0299 B=EXJ
0300 IF(ICNTR.EQ.1) EFZ=-R
0301 Q6= (-0.1*EXP5*HM3*(210*AB2*ABY2*ABZ2*HM2*C+2*ABY*8*EFY*(2*ABZ*EFZ
0302 *A*(4*C2*AB6*HM3+3*AB4*HM1-6*AB5*HM2*C)-(4*C2*(6*AB4*ABZ2
0303 *HM3-3*AB5*ABZ2*HM2-RAB6*HM3)-8*C3*ABZ2*(RAB5*HM4-HAB6*HM3)+
0304 15*AB92*ABZ2*HM1-30*AB83*ABZ2*HM2*C+3*AB4*HM1*(2*ABZ2*C-1))+6

```

```

* RAB5*HM2*(C))+2*ABZ*EFY*(4*C2*(6*RAB4*ARY2*HM3-3*PAB5*ABY2*
* HM2-RAB6*HM3)-8*C3*AEY2*(RAE5*HM4-RAB6*HM3)+15*RAE5*HM2*(C)*A-(
* 30*RAB3*ABY2*HM2*(C)+3*RAB4*HM1*(2*ABY2*(C-1)+6*RAE5*HM2*(C)*A-(
* 16*(RAB4*HM5-2*RAB5*HM4+RAB6*HM3)*C4*ABY2*ABZ2+4*C2*(45*RAB2*
* ABY2*ABZ2*HM3-30*RAB3*ABY2*ABZ2*HM4+2*3*RAE4*(ABY2*(ABZ2*HM1-2*
* HM3)-2*ABZ2*HM3)+3*RAB5*(ABY2*ABZ2)*HM2+RAB6*HM3)-8*C3*(10*
* RAB3*ABY2*ABZ2*HM4-12*RAE4*ABY2*ABZ2*HM3+RAB5*(ABY2*(3*ABZ2*
* HM2-HM4)-ABZ2*HM4)+ABY2*FAE6*HM3+ABZ2*ABZ2*ABZ2*ABZ2*(ABY2
* *(4*ABZ2*(C-1)-ABZ2)*HM1+30*RAB3*(ABY2*ABZ2)*HM2*(C-3*RAB4*(2*
* ABY2*(C+2*ABZ2*(C-1)*HM1-6*RAE5*HM2*(C+105*ABY2*ABZ2*HM1)))/(8*
* C5*AB9*EXP0)

```

GINT=C6*EXPREF*S03

0275
0276
0277
0278
0279

0280

RETURN

GO TO (115,572,573),I TYPE

IF(RAB.LT.1.D-10) GO TO 574

```

ANS5=-8*((15*ABX2-ABY2)*RAB5+10*RAB3*(ABX2*ABY2-ABX4))*C3+4*C4
* RAB5*(ABX2*ABY2-ABX4))*HM4+16*HM5*(C4*RAB4*(ABX2*ABY2-ABX4)
* ANS4=2*ABX*EFY*(B*(15*HM1*RAE2*ABY2+6*HM1*RAE4*AEY2*(C+6*HM1*
* RAB4-12*HM2*RAE5*ABY2-30*HM2*RAE3*ABY2*(C-12*HM2*RAE5*(C+24*
* HM3)*C2*RAB4*ABY2+8*HM3*(C2*RAB6+8*HM3)*C3*ABY2*ABZ2+8*HM4*(C3*
* RAB5*ABY2)-3*HM1*(5*FAE2*ABY2+2*RAB4*(ABY2*(C+1))*A+6*HM2*(2*
* C2*RAE5*ABY2+5*RAE3*ABY2*(C+2*RAD5*(C)*A-8*HM3*(C2*(3*RAE4*
* ABY2+RAB6)+C3*ABY2*(RAB6)+8*HM4*(C3*RAE5*ABY2*(C-2*EFX*ABX3*(B*
* (15*HM1*RAE2+6*HM1*RAE4*(C-12*HM2*RAE5*ABY2-30*HM2*RAE3*(C+24*HM3
* *C2*RAB4+8*HM3*(C3*RAE6-8*HM4*(C3*RAE5)*C)-8*HM3*(C3*RAE6)+8
* C)+6*HM2*(C2*RAE5*ABY2+5*RAE3*(C)-8*HM3*(C3*RAE6)+8*HM3*(C3*
* *HM4*(C3*RAE5*(C+2*HM1*RAE4-6*HM2*RAE5*(C+4*HM3*(C2*RAB6)*B*
* EFY2*(ABX2-ABY2))*A+3*(5*((4*ABY2*(C+5)*ABX2-4*ABX4*(C-ABY2)*
* RAB2+2*(4*ABX2*(C-1)*RAB4+4*(C2*RAE4*(ABX2*ABY2-ABX4)+35*ABX2*
* ABY2-35*ABX4)*HM1-6*(4*(5*RAE3*(ABX2*ABY2-ABX4)+2*RAE5*ABX2)*
* C2+5*(5*ABX2-ABY2)*RAB3*(C+4*C3*RAE5*(ABX2-ABX4)-2*RAE5*(C
* )*HM2+4*((16*(5*ABX2-ABY2)*RAB4+45*RAE2*(ABX2*ABY2-ABX4)-2*
* RAB6)*C2+8*(3*RAE4*(ABX2*ABY2-ABX4)+ABX2*RAE6)*C3+4*C4*RAE6*(
* ABX2*ABY2-ABX4))*HM3+ANS5

```

ANS3=-ANS4

ANS2=210*RAE*HM2*(ABX2*ABY2-AEX4)*C+ANS3

ANS1=PI*ANS2*EXP5M

G7=ANS1/(8*C5*RAE9)*EXPREF

GINT=Q7*SQ3/2.D0

RETURN

IF(RAB.LT.1.D-10) GO TO 575

```

ANS4=-((2*ABY*EFY*(15*HM1*RAE2*ABX2+6*HM1*RAE4*ABX2*(C+6*HM1*
* RAB4-12*HM2*RAE5*ABX2-30*HM2*RAE3*ABX2*(C-12*HM2*RAE5*(C+24*
* HM3)*C2*RAE4*ABX2+9*HM3*(C2*RAE6+8*HM3*(C3*ABX2*RAE6-8*HM4*(C3*
* RAB5*ABX2))*B-A)-2*B*(EFY*ABY3*(15*HM1*RAE2+6*HM1*RAE4*(C-12*
* HM2*(C2*RAE5-30*HM2*RAE3*(C+24*HM3*(C2*RAE4+8*HM3*(C3*RAE6-8*HM4*
* C3*RAE5)+6*HM1*RAE4*EFY2*(ABX2-ABY2))*A-12*HM2*RAE5*EFY2*(ABX2
* -ABY2)*C4+3*HM3*(C2*EFY2*RAE6*(ABX2-ABY2))*A)+2*EFY*ABY3*(15
* *HM1*RAE2+6*HM1*RAE4*(C-12*HM2*RAE5-30*HM2*RAE3*(C+24*HM3*(C2
* *RAE4+9*HM3*(C3*RAE6-8*HM4*(C3*RAE5)*C)+2*RAE5*ABX2*ABY2*
* -4*C2*RAE4*ABY4+20*RAE2*ABX2*ABY2*(C+5*HM1*(4*ABX2*RAE4*ABX2*ABY2
* C+25*RAE2*ABY2+8*RAE4*ABY2*(C-2*RAE4+35*ABX2*ABY2-35*ABY4)-6*
* HM2*(4*(C2*(15*RAE3*(ABX2*ABY2-ABY4)+2*RAE5*ABY2)+4*C3*RAE5*(
* ABX2*ABY2-ABY4))-5*RAE3*(C*(AEX2-5*ABY2)-2*RAE5*(C*(C2*(
* 45*RAE2*(ABX2*ABY2-ABY4)-6*RAE4*(ABX2-5*ABY2)-2*RAE6)+8*(C3*(3
* *RAE4*(ABX2*ABY2-ABY4)+AEY2*RAE6*(ABX2*ABY2-ABY4))
* -8*HM4*(C3*(10*RAE3*(ABX2*ABY2-ABY4)-RAE5*(ABX2-5*ABY2))+4*C4
* *RAE5*(ABX2*ABY2-ABY4))+16*HM5*(C4*RAE4*(ABX2*ABY2-ABY4))
* ANS3=210*RAE*HM2*(ABX2*ABY2-ABY4)*C+ANS4

```

0281
0282
0283
0284
0285
0286
0287
0288

0289

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QINT

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```

0290 ANS2=PI*ANS3*EXP5M
0291 ANS1=-ANS2
0292 Q7=ANS1/(8*C5*RAE9)*EXPREF
0293 QINT=Q7*S03/2.00
0294 RETURN
0295 HVI=-HMI
0296 QINT=2.*PI*HMI/15.*S02
0297 RETURN

C < PX / QR / PY >
580 IF(RAB.LT.1.0-10) GO TO 581
    IF(ITYPE.EQ.2) GO TO 583
    A=FXJ
    P=FXI
    IF(JCINT.H.EQ.1) EFZ=-R
    GO TO 582
583 A=FXI
    P=EXJ
    IF(ICNTR.EQ.1) EFZ=-R
    IF(ICNTR.EQ.1)
        Q8=((-PI*(210*RAE*ABY*HM2+C*ABX2+ABY*(2*ABX*EFX*8*(8*RAE6*HM3*
        *RAB2)*HMI+6*(5*C*RAE3+2*(2*RAE5)*HM2-2*HM3*C2*RAE4+8*HM4*C3*
        *RAB5)-8*RAE6*HM3*(EFY*(C2-2*C3*ABX2)*A-(C3-2*C4*ABX2))*2*EFY*
        *(3*HMI*(15*RAE2*ABX2-RAB4)+2*C*RAE4*ABX2)-6*HM2*((5*RAE3*ABX2
        *-RAB5)*C+2*C2*RAE5*AEX2)+2*HM3*C2*RAE4*ABX2-8*HM4*C3*RAE5*
        *ABX2)*A-3*HMI*(2*(10*RAE3*ABX2-RAB4)*C+4*C2*RAE4*ABX2-5*RAE2*
        *35*AEX2)+6*HM2*(2*(10*RAE3*ABX2-2*RAE4)*C2+9*C3*RAE4*ABX2)+8*HM4*
        *ABX2)-12*HM3*((15*RAE2*AEX2-2*RAE4)*C2+4*C4*RAE5*ABX2)-16*HM5*
        *C4*RAE4*ABX2)+
        *HMI*ABX*EFX*3*RAE6*HM3*C2+8*RAE6*HM3*C3*ABX2+6*HMI*C*RAE4*ABX2
        *H2*C*RAE5-4*RAE6*HM3*C2+3*HM1*RAE4-30*HM2*C*RAE3*ABX2+6*HM2*C*RAE5-
        *12*HM2*C2*RAE5*ABX2+24*HM3*C2*RAE4*ABX2-8*HM4*C3*RAE5*ABX2))
        /((8*RAE9*EXP0*EXP5*C5)
    QINT=C8*FXPREF*S03
    RETURN
581 QINT=2.*PI*HMI/15.*S02
    RETURN
    END

```

```

0309
0310
0311
0312

```

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DS1

```

0001 REAL FUNCTION DS1*(R)
0002 IMPLICIT REAL*(A-H,O-Z)
0003 COMMON/INT/C,CK,RAB,OKG
0004 COMMON/POT/POTCK(15),IPCT
0005 DATA PEACH,DALGAR/ SHPEACH,8+DALGARND/
0006 IF(R.EQ.0.0D0) GO TO 100
0007 C*** TAKE OUT GO TO 98 FOR PEACH'S CUTOFF
0008 C
0009 GC TO 98
0010 C*** PEACH'S CUTOFF FUNCTION ***
0011 CUT=OK*R
0012 CUT=1.D0-DEXP(-CUT)*(1.D0+CUT*(1.D0+.5D0*CUT))
0013 POTCK(1)=PEACH
0014 GC TO 99
0015 C*** CUT=(OK*R)**3
0016 POTCK(1)=DALGAR
0017 IF(CUT.GT.1.D-10) CUT=1.D0-DEXP(-CUT)
0018 IF(RAB.LT.1.D-10) GO TO 200
0019 TGRAB=2.*C*RAB*R
0020 IF(TGRAB.LT.1.D0) GO TO 199
0021 EXP1=DEXP(-C*(RAB-R)**2)
0022 EXP2=DEXP(-C*(RAE+R)**2)
0023 DS1=CUT*(EXPRM-EXFRP)/(EXP1+EXP2)
0024 RETURN
0025 U/(R*R)
0026 DS1=CLT*DSINH(TGRAB)*DEXP(-C*(R*R+RAB*R))
0027 RETURN
0028 U/(R*R)
0029 RETURN
0030 DS1=CLT*R*DEXP(-C*R*R)
0031 RETURN
0032 DS1=0.0D0
0033 RETURN
0034 END

```

```

0001 REAL FUNCTION DS2*(R)
0002 IMPLICIT REAL*(A-H,O-Z)
0003 COMMON/INT/C,CK,RAB,DNG
0004 COM/4/N/P/T/POTCK(15),IPCT
0005 DATA PEACH,DALGAR/ 5*PEACH,8+DALGARND/
0006 IF(R.EQ.0.0DC) GC TC 100
0007 TGPAB=2.*C*RAB*R
C*** TAKE OUT GC TC 98 FOR PEACH'S CUTCFF
C
C*** PEACH'S CUTOFF FUNCTION **
97 CUTE=D*K*R
CUTE=1.D0-DEXP(-CUT)*(1.D0+CUT*(1.D0+.500*CUT))
POTCK(2)=PEACH
GO TO 99
98 CUTE=(CK*R)**2
POTCK(2)=DALGAR
IF(CUT.GT.1.D-10) CUTE=1.DC-DEXP(-CUT)
99 IF(TGRAB.LT.1.D0) GC TC 199
EXPRM=DEXP(-C*(RAB-R)**2)
EXPRP=DEXP(-C*(RAB+R)**2)
DS2=CUTE*(EXPRM+EXPRP)/(R**2.)
RETURN
199 DS2=CUTE*DCOSH(TGRAB)*DEXP(-C*(R*R+RAB*RAB))/R
RETURN
DS2=0.0D0
100 RETURN
END

```

```

0001 REAL FUNCTION DS3*(R)
0002 IMPLICIT REAL*(A-H,O-Z)
0003 COMMON/INT/C,DK,RAB,OKQ
0004 COMMON/FUT/POTCK(15),IPCT
0005 DATA PEACH,DALGAR/5,5HEACH,RMDALGARND/
0006 IF(R.EQ.0.0D0) GO TO 100
0007 TGRADE=2.*C*RAB*R
      C
      C*** TAKE OUT GO TC 98 FOR PEACH'S CUTOFF
      C
      C*** PEACH'S CUTOFF FUNCTION ***
0008 97 CUT=DK*R
0009 CUT=1.0D0-DEXP(-CUT)*(1.0D0+CUT*(1.0D0+.5D0*CUT))
0010 POTCK(1)=PEACH
0011 GO TO 99
0012 CUT=(DK*R)**3
0013 POTCK(1)=DALGAR
0014 IF(CUT.GT.1.D-10) CUT=1.0D0-DEXP(-CUT)
0015 99 IF(TGRAD.LT.1.D0) GO TO 199
0016 EXPRM=DEXP(-C*(RAB-R)**2)
0017 EXPRP=DEXP(-C*(RAB+R)**2)
0018 DST=CLT*(EXPRM-EXPRP)/2.
0019 RETURN
0020 DS3=CUT*DSINH(TGRAB)*CEXP(-C*(R*R+RAB*RAB))
0021 RETURN
0022 DS3=0.0D0
0023 RETURN
0024 END

```

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DS4

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```

0001 REAL FUNCTION DS4*(R)
0002 IMPLICIT REAL*(A-H,O-Z)
0003 COMMON/INT/C,DK,RAB,DKQ
0004 COMMON/POY/POTCK(15),IPCT
0005 DATA PEACH,DALGAR/ SHEEACH,8HDCALGARND/
0006 IF(R.EQ.0.000) GO TO 100
0007 TGRAB=2.*C*RAB*R
      C*** TAKE OUT GO TO 98 FOR PEACH'S CUTOFF
      C
      C*** PEACH'S CUTOFF FUNCTION ***
0008   97 CUT=DK*R
0009   CUT=1.00-DEXP(-CUT)*(1.00+CUT*(1.00+.5D0*CUT))
0010   POTCK(4)=PEACH
0011   GO TO 99
0012   98 CUT=(DK*R)**3
0013   POTCK(4)=DALGAR
0014   IF(CUT.GT.1.0-10) CUT=1.00-DEXP(-CUT)
0015   IF(TGRAB.LT.1.00) GO TO 199
0016   EXPRM=DEXP(-C*(RAB-R)**2)
0017   EXPRP=DEXP(-C*(RAB+R)**2)
0018   DS4=CLT*(EXPRM+EXPRP)**5/2.
0019   RETURN
0020   109 DS4=CUT*DCOSH(TGRAB)*[EXP(-C*(R+RAB*RAB))]*R
0021   RETURN
0022   100 DS4=0.0D0
0023   RETURN
0024   END

```

```

0001 REAL FUNCTION DSS*(P)
0002 IMPLICIT REAL*8(A-H,O-Z)
0003 COMMON/INT/C,DK,RAB,DKQ
0004 COMMON/FACT/PTCK(15),IPCT
0005 DATA PEACH,DALGAR,SHPEACH,8HDALGARNC/
0006 IF(R,EQ,0.000) GO TO 100
0007 C*** TAKE OUT GO TO 98 FOR PEACH'S CUTOFF
0008 C
0009 C*** PEACH'S CUTOFF FUNCTION ***
0010 CUT=DKQ*R
0011 CUT=1.00-DEXP(-CUT)*(1.00+CUT*(1.00+CUT*(.500+CUT/6.00)))
0012 PTCK(5)=PEACH
0013 GO TO 99
0014 C*** CUT=(DK*R)**4
0015 PTCK(5)=DALGAR
0016 IF(CUT.GT.1.0-10) CUT=1.00-DEXP(-CUT)
0017 IF(RAB.LT.1.0-10) GO TO 200
0018 TGRAB=2.*C*RAB*R
0019 IF(TGRAB.LT.1.00) GO TO 199
0020 EXPR4=DEXP(-C*(RAB-R)**2)
0021 EXPRP=DEXP(-C*(RAB+R)**2)
0022 DSS=CUT*(EXPRM-EXPRP)/(R**4*2.)
0023 RETURN
0024 U R***
0025 DSS=CUT*DSINH(TGRAB)*DEXP(-C*(R*R+RAB*R))/
0026 RETURN
0027 PETURN
0028 DSS=CUT*R*DEXP(-C*R*R)
0029 RETURN
0030 DSS=0.000
0031 RETURN
0032 END

```

```

0001 REAL FUNCTION DS6*(R)
0002 IMPLICIT REAL*(A-H,O-Z)
0003 COMMON/INT/C*DK,RAB,DKQ
0004 COMMON/PUT/POTCK(15),IFCT
0005 DATA PEACH,DALGAR/ SHPEACH,8FDALGARND/
0006 IF(R.EQ.0.000) GO TO 100
0007 TGRAB=2.*C*RAB*R
      C*** TAKE OUT GO TO 98 FOR PEACH'S CUTOFF
      C
      GO TO 98
0008 C*** PEACH'S CUTOFF FUNCTION ***
0009 CUT=DKQ*R
0010 CUT=1.00-DEXP(-CUT)*(1.00+CUT*(1.00+CUT*(.500+CUT/6.00)))
0011 POTCK(6)=PEACH
0012 GC TO 99
0013 CUT=(DK*R)**4
0014 IF(CJT.GT.1.0-10) CUT=1.00-DEXP(-CUT)
0015 POTCK(6)=DALGAR
0016 IF(TGRAB.LT.1.00) GO TO 159
0017 EXPRM=DEXP(-C*(RAB-R)**2)
0018 EXPRP=DEXP(-C*(RAB+R)**2)
0019 DS6=CUT*(EXPRM+EXPRP)/(R**3*2.)
0020 RETURN
      U/R**3
0021 DS6=CUT*DCOSH(TGRAB)*DEXP(-C*(R*R+RAB*RAB))
0022 RETURN
0023 DS6=0.000
0024 END

```

```

0001 REAL FUNCTION DS7*(P)
0002 IMPLICIT REAL*(A-H,C-Z)
0003 COMMON/INT/C,DK,RAB,DKQ
0004 COMMON/PUT/POTCK(15),IPCT
0005 DATA PEACH,DALGAR,SHFEACH,8*DALGARNC/
0006 IF(R.EQ.0.000) GO TO 100
0007 TGRAB=2.*C*RAB*R
C*** TAKE OUT GO TC 98 FOR PEACH'S CUTOFF
C
0008 GC TO 98
C*** PEACH'S CUTOFF FUNCTION ***
97 CUT=DKQ*R
CUT=1.00-DEXP(-CUT)*(1.00+CUT*(.500+CUT/6.00))
POTCK(7)=PEACH
GO TO 99
98 CUT=(DK*R)**4
POTCK(7)=DALGAR
IF(CUT.GT.1.0D-10) CUT=1.00-DEXP(-CUT)
99 IF(TGRAB.LT.1.00) GO TC 199
EXPRM=DEXP(-C*(RAB-R)**2)
EXPRP=DEXP(-C*(RAB+R)**2)
DS7=CLT*(EXPRM-EXPRP)/(R**2.)
RETURN
199 DS7=CUT*DSINH(TGRAB)*CEXP(-C*(R*R+RAB*RAB))
U/(R*R)
RETURN
100 DS7=0.000
RETURN
END
0021
0022
0023
0024

```



```

0001 REAL FUNCTION DS8*(R)
0002 IMPLICIT REAL*(A-H,O-Z)
0003 COMMON/INT/C,CK,RAB,DKG
0004 COMMON/POT/POTCK(15),IPCT
0005 DATA PEACH,DALGAR/ 5HPFACH,8FDALGARNO/
0006 IF(R.EQ.0.000) GO TO 100
0007 TGRAB=2.*C*RAB*R
      C*** TAKE OUT GO TO 93 FOR PEACH'S CUTOFF
      GO TO 93
C*** PEACH'S CUTOFF FUNCTION ***
97 CUT=DKQ*R
  CUT=1.00-DEXP(-CUT)*(1.00+CUT*(1.00+CUT*(.500+CUT/6.00)))
  POTCK(9)=PEACH
  GO TO 93
98 CUT=(DK*R)**4
  POTCK(9)=DALGAR
  IF(CUT.GT.1.0-10) CUT=1.00-DEXP(-CUT)
  IF(TGRAB.LT.1.00) GO TO 155
0015 EXPRM=DEXP(-C*(RAB-R)**2)
0016 EXPRP=DEXP(-C*(RAB+R)**2)
0017 DS8=CUT*(EXPRM+EXPRP)/(R**2.)
0018 RETURN
0019 DS8=CLT*DCOSH(TGRAB)*DEXP(-C*(R*R+RAB*RAB))/R
0020 RETURN
0021
0022 100 DS8=0.000
0023 RETURN
0024 END

```

```

0001 REAL FUNCTION DS9*(R)
0002 IMPLICIT REAL*8(A-H,D-Z)
0003 COMMON/INT/C,CK,RAB,OKG
0004 COMMON/POT/PCTCK(15),IPCT
0005 DATA PEACH,DALGAR,SHPEACH,8HDALGARND/
0006 IF(R,E0.0.000) GO TC 100
0007 TGRAB=2.*C*RAB*R
      C*** TAKE OUT GO TO 98 FOR PEACH'S CUTOFF
      C
      GO TO 98
0008 C*** PEACH'S CUTOFF FUNCTION ***
0009 97 CUT=DKGR
0010 CUT=1.D0-DEXP(-CUT)*(1.D0+CUT*(1.D0+CUT*(.5D0+CUT/6.D0)))
0011 POTCK(9)=PEACH
      GO TO 99
0012 98 CUT=(DKR)**4
0013 POTCK(9)=DALGAR
      IF(CUT.GT.1.D-10) CUT=1.D0-DEXP(-CUT)
0014 IF(TGRAB.LT.1.D0) GO TO 159
0015 99 EXPRM=DEXP(-C*(RAB-R)**2)
0016 EXPRP=DEXP(-C*(RAB+R)**2)
0017 DS9=CUT*(EXPRM-EXPRP)/2.
0018 RETURN
0019 DS9=CLT*D SINH(TGRAB)*DEXP(-C*(R+RAB*RAB))
0020 199
0021 100 RETURN
0022 DS9=0.0D0
0023 RETURN
0024 END

```

```

0001 SUBROUTINE ITROMB(FCN,HIN,ERT,NAPP,VINT,IERR,X0)
0002 IMPLICIT REAL*8 (A-H,O-Z)
0003 DIMENSION AUX(10)
0004 COMMON/ERR/NERR
C EVALUATES EXTERNAL STATEMENT FOR FCN
C BY TRAPEZOIDAL RULE WITH ROMBERG EXTRAPOLATION
C PROG MAY RESULT IN ERROR IN LANDS ON SUCCESSIVE NODES OF FCN(X)
C HIN IN INTERVAL AT WHICH 1ST INTEGRATION DONE
C ERT IS MAX ERROR DESIRED
C NAPP IS MAX NC TIMES INTEGRAL EVALUATED BY TRAP. MUST BE .LE.10
0005 IERR=0
0006 NERR=0
0007 RO=0.0D0
0008 V=0.0D0
0009 HS=HIN
0010 H=HS
0011 X=X0
0012 A=.5D0*FCN(X)
0013 DO 250 N=1,NAPP
0014 X=X+HS
0015 NINT=0
0016 NINT=NINT+1
0017 T=FCN(X)
0018 IF(NERR.NE.0) GO TO 400
0019 IF(DABS(T).LE.ERT*DABS(A/NINT)) GO TO 100
0020 A=A+T
0021 GC TO 50
0022 A=A+T
0023 IF(RO.NE.0.0D0) GC TO 150
0024 NINT=NINT+1
0025 X=X+HS
0026 T=FCN(X)
0027 IF(NERR.NE.0) GO TO 400
0028 IF(DABS(T).LE.ERT*DABS(A/NINT)) GO TO 101
0029 A=A+T
0030 GC TO 50
0031 IF(X.LT.RO) GC TO 50
0032 AUX(N)=H*A+.5D0*V
0033 FCRMAT(1H,2FN,15,5X,7F,AUX(N)=D27.16)
0034 IF(DABS(AUX(N)-V).LE.ERT*CABS(V)) GO TO 251
0035 V=AUX(N)
0036 IF(RO.EQ.0.0D0) RO=X
0037 IF(N.EQ.NAPP) GO TO 250
0038 HS=H
0039 H=.5D0*H
0040 X=X+H
0041 A=FCN(X)
0042 CONTINUE
0043 FORMAT(1H,12HMAX VALUE X=D13.6)
0044 D=1.0D0
0045 NK=NAPP-1
0046 DC 300 K=1,NK
0047 D=A.*C
0048 NJ=NAPP-K
0049 Y=AUX(NJ+1)
0050 DO 300 J=1,NJ
0051 NA=NAPP-(K+J)+1
0052 AN=AUX(NA)

```

```

0053 AUX(NA)=Y+(Y-AN)/(O-1.)
0054 IF(DABS(AUX(NA)-Y).LE.ERI*DABS(Y)) GC TO 301
0055 Y=AN
0056 CCNTINJE
0057 IERR=1
0058 IMPLIES NAPP NOT LARGE ENOUGH
0059 SFRR=AUX(NA)-AUX(NA+1)
0060 WRITE(6,500) SFRR,AUX(NA)
0061 FCRMAT(1H,5X,6HEXOR=,C27.16,5X,5HVINT=,D27.16)
0062 VINT=AUX(NA)
0063 FCRMAT(1H,10X,19FITRCMB CONV WITH K=.15,5X,3HNK=,15)
0064 RETURN
0065 VINT=AUX(N)
0066 RETURN
0067 IERR=NERR
0068 IF(NERR.NE.3) GO TO 401
0069 TR0=FCN(X-HS)
0070 NERR=C
0071 FCRMAT(1H,10HFCN AT R0=,D27.16)
0072 A=AT
0073 GO TO 101
0074 VINT=H*A+.5*V
0075 WRITE(6,602) NERR
0076 FCRMAT(1H0,13FITRCMB ERROR=,15//)
0077 RETURN
END

```

```

0001 SUBROUTINE NDQG32(XMIN,XMAX,FCN,VINT,N)
0002 IMPLICIT REAL*8(A-H,C-Z)
0003 EXTERNAL FCN
0004
0005 C
0006 C
0007 C
0008 C
0009 C
0010 C
0011 C
0012 C
0013 C
0014 C

```

NDQG32(XMIN,XMAX,FCN,VINT,N)
 IMPLICIT REAL*8(A-H,C-Z)
 EXTERNAL FCN
 DCES 32 POINT GAUSSIAN QUADRATURE N TIMES ON INTERVAL
 XMIN TO XMAX IN EQUAL SUBINTERVALS
 VINT=0.000
 STEP=(XMAX-XMIN)/N
 XMINI=XMIN
 DC 100 IN=1,N
 XMAXI=XMINI+STEP
 CALL DQ32(XMINI,XMAXI,FCN,VINTI)
 VINT=VINT+VINTI
 XMINI=XMAXI
 RETURN
 FORMAT(1H ,10X,6HVINTI=E27.16)
 END

```

0001 REAL FUNCTION RINT#8(IDUM)
0002 IMPLICIT REAL*8(A-H,C-Z)
0003 PFAL#8 K,K2,K3,K4,K5,K6
0004 REAL#1 SEC
0005 LOGICAL INTC,LA
0006 EXTERNAL GS1,GS2,CS3,CS4,GS5,GS6
0007 COMMON/INT/C,DK,RAB,DRG,IITYPE
0008 COMMON/SCLR/EXI,FXJ,IITYPE,JTYPE,ICNTR,JCNTR,R,K,CUT2,CUT3,
    U ALPHA,ALPHAC,AP(4),LA(6),RINTG(6)
0009 COMMON/POY/PCTCK(15),IPCT
0010 DATA PI,RTPI/3.14159265358979D0,1.7724538E090551D0/
0011 DATA NAPP,STPEM/3,1000,C0/
0012 DATA NGQ/6/
0013 C*****WARNING: INTERVALS FOR GAUSSIAN QUAD DECREASED*****
0014 PHI(X)=DFRF(X)
0015 SINH(X)=DSINH(X)
    CSH(X)=DCCSH(X)
    C PROGRAM USES INTEGRAL EXPRESSIONS OBTAINED FROM REDUCE
    C IITYPE=1,S
    C 2,PX
    C 3,PY
    C 4,PZ: Z ASSUMED TO BE ALONG DIRECTION OF BOND
    C ICNTR=1 FOR A, THE CLOSEST SHELL ATOM ON WHICH EFFECTIVE POTENTIAL
    C IS CENTERED
    C 2 FOR ATOM B, NON-CLOSED SHEL
    C
    IITYPE=IITYPE
    DO 99 I=1,6
    98 RINTG(I)=0.0D0
    R1=0.0D0
    R2=0.0D0
    R3=0.0D0
    R4=0.0D0
    R5=0.0D0
    R6=0.0D0
    IF(IPGT.EQ.0) GO TC 100
    DK=CUT2
    DK0=CUT3
    GO TO 99
    CK=K
    100 RINT=C.0D0
    99 IF(IITYPE.LE.4.AND.JTYPE.LE.4) GC TO 101
    WRITE(6,600) IITYPE,JTYPE
    600 FORMAT(1H,25H*****EFCR***** /
    U 1H,6H IITYPE=,15,5X,6H JTYPE=,15 /
    U 1H,24H ONLY TYPE .LE.4 ALLOWED /
    U 1H,20H***** /
    RETURN
    101 IF(IITYPE.FQ.JTYPE.OR.(IITYPE.EQ.1.AND.JTYPE.EQ.4).OR.(IITYPE.EQ.4
    U .AND.JTYPE.EQ.1)) GO TO 102
    102 RETURN
    C=EXI+EXJ
    EXPO=1.0
    IF(ICNTR.EQ.JCNTR) GC TC 110
    EXPREF=DEXP(-EXI*EXJ**2/C)
    IF(EXPREF.EQ.0.0D0) RETURN
    IF(ICNTR.EQ.1) GC TC 105
    PAB=EXI#H/C
    GC TO 150

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0045 105 RAB=EXJ*R/C
0046 GO TO 150
0047 110 EXPREF=1.D0
0048 IF(ICNTR.EQ.1) GO TO 115
0049 RAB=R
0050 GC TO 150
0051 115 WAR=0.000
0052 150 PTC=DSORT(C)
0053 IF(IITYPE.NE.1.OR.JTYPE.NF.1).AND.IITYPE.NE.JTYPE.AND
      U RAB.LT.1.D-10) GO TO 200
C DEF
EXP1 = DEXP(K**2/(4*C))
EXP2 = DEXP(K*RAB)
EXP5M=DEXP(-C*RAB**2)
RAB = RAB - K/(2*C)
RAB = RAB + K/(2*C)
IF(LA(1)) GC TO 114
PHIMC=DERFC(-RTC*RAM)
PHIPC=DERFC(RTC*RAM)
PHIOC=PHIPC
EXP22=EXP2**2
114 C2=C*C
C3=C2*C
C4=C2*C2
C5=C4*C
RAB2=RAB*RAB
RAB3=RAB*RAB2
K2=K*K
K3=K2*K
K4=K2*K2
RAP2=RAB**2
RAP3=RAB2*RAP
KAM2=RAM**2
RAM3=RAM2*RAM
REXP=DSORT(-DLGG(1.D-10)/C)
RMIN=DVAX1(RAB-REXP,C.0C0)
RMAX=FAB+HEXP
INTC=(C.LT..2D0.CF.(C.LE..2D0.AND.RAE.GT.10.D0)
      U .OR.(C.GE.1.D3.AND.RAB.LT..1D0))
C IF(INTC) GO TO 120
C*****WARNING: ALL INTEGRALS DONE BY DGG32
C*****REMOVE C TO GET ITROME*****
P3=3.
P5=5.
IF(RAB.GT.1.D-10) GO TO 116
P3=2.
P5=4.
116 RMAX1=DMIN1(RMAX,1.D10**(1./P3))
RMAX2=DMIN1(RMAX,1.D1C**(1./P5))
IF(.NOT.LA(1)) CALL NCOG32(RMIN,RMAX1,GS1,HM1,NGC)
IF(.NOT.LA(2)) CALL NCOG32(RMIN,RMAX2,GS2,HM2,NGQ)
GO TO 120
120 FEXP=(RAB+REXP-RMIN)/STEPM
HMIN1=(1.D8)**(1./3.)/STEPM
HMIN2=1.D8**2/STEPM
HMIN=DMIN1(HEXP,HMIN1*2**(NAPP-1)
HMIN2=DMIN1(HEXP,HMIN2)*2**(NAPP-1)
IF(.NOT.LA(1)) CALL ITROME(GS1,HMIN1,1.D-8,NAPP,HM1,IERR,RMIN)
IF(.NOT.LA(2)) CALL ITROME(GS2,HMIN2,1.D-8,NAPP,HM2,IERR,RMIN)
0081 0081
0082 0082
0083 0083
0084 0084
0085 0085
0086 0086
0087 0087
0088 0088
0089 0089
0090 0090
0091 0091
0092 0092
0093 0093
0094 0094
0095 0095
0096 0096
0097 0097

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0094 CONTINUE
0095 FORMAT(1H,4HHMU=.E15.6,SX,SHM21=.E15.6)
0100 IF(IJTYPE.NE.1.CR.JTYPE.NE.1) GO TO 200
C < S / R / S > INTEGRALS
0101 IF(RAB.LT.1.D-10) GO TO 160
C DEF R1 ETC
0102 IF(.NOT.LA(1)) R1=(2*PI*EXPREF*HM1)/(RAB*C)
0103 IF(.NOT.LA(2)) R2=(2*PI*EXPREF*HM2)/(RAB*C)
0104 IF(LA(3)) GO TO 131
0105 R3=(RTPI*PI*(K*(PHIPC*EXP22-PHIMC)+2*RAB*(PHIPC*EXP22+PHIMC)*
C)*EXP1)/(4*RAB*RTC*EXP2*C2)*EXPREF
0106 IF(LA(4)) GO TO 122
0107 R4=(-PI*(4*K*RAB*RTC*RTPI*EXP1*(PHIPC*EXP22+PHIMC)*C-8*RAB*
C*EXP2*EXP5*C2+PHIPC*FTC*RTPI*EXP1*(4*C2*RAB2*K2+2*C2))/(8*RAB*EXP2*C4)*EXPREF
0108 IF(LA(5)) GC TO 133
0109 R5=(-PI*(2*K*(8*RAB*EXP2*EXP5*C2-3*EXP1*RTC*RTPI*(2*C2*RAB2+
C)*PHIPC*EXP22-PHIMC))-6*RAB*EXP1*RTC*RTPI*(2*C2+K2*C)*
C*PHIPC*FXP22+PHIMC)-EXP1*FTC*RTPI*(PHIPC*EXP22*(8*C3*RAB3*K3)+
C*PHIMC*(8*C3*RAB3-K3)))/(16*RAB*EXP2*C5)*EXPREF
0110 IF(LA(6)) GC TO 500
0111 R6=(-RTPI*PI*EXP1*(PHIPC*EXP22-PHIMC))/(2*RAB*RTC*EXP0*EXP2*C
C)
0112 R6=R5*EXPREF
0113 GO TO 500
0114 IF(.NOT.LA(1)) R1=(2*PI*HM1)/(EXP0*C)
0115 IF(.NOT.LA(2)) R2=(2*PI*HM2)/(EXP0*C)
C DEF P3 ETC
0116 IF(LA(3)) GC TO 161
0117 R3=(-PI*(2*K*RTC-RTPI*(K2+2*C)*EXP1*PHI0C))/(2*RTC*C2)
0118 IF(LA(4)) GO TO 162
0119 R4=(-PI*(6*K*RTC*RTPI*EXP1*PHI0C*C+(RTC*RTPI*EXP1*PHI0C*K3-8*
C*C2-K2*C))/(4*C4)
0120 IF(LA(5)) GC TO 163
0121 R5=(-PI*(20*K*C2-RTC*EXP1*RTPI*PHI0C*(12*C2+12*K2*C+K4))+2*K3*
C)/(8*C5)
0122 IF(LA(6)) GC TO 500
0123 R6=(-PI*(K*RTPI*EXP1*PHI0C-2*RTC))/(RTC*C)
0124 GC TO 500
0125 IF(RAB.NE.0.CR.IJTYPE.EG.JTYPE) GO TO 201
0126 RINT=C.000
0127 RETURN
0128 CC=C3*C3
0129 RAD4=RAB2*RAB2
0130 RAB5=RAB4*RAB
0131 IF(RAB.LT.1.D-10) GO TO 300
C IF(INTC) GO TO 170
0132 RMAX1=DMIN1(RMAX,1.D10**.5)
0133 RMAX2=DMIN1(RMAX,1.D1C**.25)
0134 IF(.NOT.LA(1)) CALL NCG32(RMIN,RMAX1,GS3,HM2,NGQ)
0135 IF(.NOT.LA(2)) CALL NCG32(RMIN,RMAX2,GS4,HM2,NGQ)
0136 GC TO 171
0137 HDEN1=1.D4/STEPM
0138 HDEN2=1.D2/STEPM
0139 PIN1=DMIN1(HEXP,HDEN1)*2*(NAPP-1)
0140 PIN2=DMIN1(HEXP,HDEN2)*2*(NAPP-1)
0141 IF(.NOT.LA(1)) CALL ITROWB(GS3,HIN1,1.D-8,NAPP,HM2,IERR,RMIN)
0142 IF(.NOT.LA(2)) CALL ITREME(GS4,PIN2,1.D-8,NAPP,HM2,IERR,RMIN)
0143 CONTINUE

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0144 61R  FORMAT(1H,4HMM2=.E15.6,5X,SHMM22=.E15.6)
0145  IF(IJTYPE.NE.1.AND.IJTYPE.NE.1) GO TO 300
0146  /R / D > INTEGRALS
0147  ABX=BAR
0148  EFX=ER
0149  IF(ICNTR.EQ.JCNTR) GO TO 202
0150  IF(ICNTR+IJTYPE.NE.2.AND.JCNTR+IJTYPE.NE.2) EFX=-R
0151  GO TO 203
0152  EFX=0.002
0153  IF(IJTYPE.EQ.4) B=EXJ
0154  IF(IJTYPE.EQ.4) B=EXI
0155  IF(ICNTR.EQ.JCNTR) GO TO 210
0156  C OFF P1 ETC
0157  IF(.NOT.LA(1)) R1=(P1*(2*RAE*C*ABX*HM2-2*0*BAR2*EFX*HM1-2
0158  *C*PAR2*ABX*HM1-ABX*HM1))/(
0159  *C*PAR2*ABX*HM1-ABX*HM1)/(
0160  *C*PAR2*ABX*HM1-ABX*HM1)/(
0161  *C*PAR2*ABX*HM1-ABX*HM1)/(
0162  *C*PAR2*ABX*HM1-ABX*HM1)/(
0163  *C*PAR2*ABX*HM1-ABX*HM1)/(
0164  *C*PAR2*ABX*HM1-ABX*HM1)/(
0165  *C*PAR2*ABX*HM1-ABX*HM1)/(
0166  *C*PAR2*ABX*HM1-ABX*HM1)/(
0167  *C*PAR2*ABX*HM1-ABX*HM1)/(
0168  *C*PAR2*ABX*HM1-ABX*HM1)/(
0169  *C*PAR2*ABX*HM1-ABX*HM1)/(
0170  *C*PAR2*ABX*HM1-ABX*HM1)/(
0171  *C*PAR2*ABX*HM1-ABX*HM1)/(
0172  *C*PAR2*ABX*HM1-ABX*HM1)/(
0173  *C*PAR2*ABX*HM1-ABX*HM1)/(

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0174      1/6      RAB3*C2)
0175      IF(LA(3)) GO TO 211
0176      R3= (PI*ABX*(K*(PHIPC*RTPI*EXP1*(2*RAB2*C-1))*EXP22-RTPI*EXP1*
0177      PHIMC*(2*RAB2*C-1))-4*EXP2*RAB*RTC*EXP5M)+PHIPC*RTPI*EXP1*RAB*
      K2*EXP22*RTPI*EXP1*RAB*PHIMC*K2)/(8*EXP2*RTC*C3*RAB3)
0178      IF(LA(4)) GO TO 212
0179      R4= (-PI*ARX*(2*K*RTIC*RTPI*EXP1*(RAB*(PHIPC*EXP22+PHIMC)*C+2*
      PHIPC*C2*RAB3*EXP22+2*PHIMC*C2*RAB3)+RAB*(PHIPC*RTC*RTPI*EXP1
      *K3*EXP22+(RTC*RTPI*EXP1*PHIMC*K3-4*EXP2*(2*C2+K2*C)*EXP5M))+
      PHIPC*RTC*RTPI*EXP1*(4*RAB2*C-1)*K2+4*C2*RAB2-2*C)*EXP22-RTC
      *RTPI*EXP1*PHIMC*((4*RAB2*C-1)*K2+4*C2*RAB2-2*C))/(16*EXP2*
      C5*RAB3)
0180      IF(LA(5)) GO TO 213
0181      R5= (-PI*ARX*(2*K*(12*RAB*EXP2*EXP5M*C2-EXP1*RTC*RTPI*(PHIPC*
      EXP22-PHIMC)*(12*C2*RAE2+4*C3*RAE4-3*C)+8*EXP2*EXP5M*C3*RAB3)
      -RAB*(EXP1*RTC*RTPI*(PHIPC*EXP22+PHIMC)*(6*K2*C+K4))-4*EXP2*
      EXP5M*K3*C)-EXP1*RTC*RTPI*(PHIPC*EXP22*(12*C2*K2*RAB3+16*C3*
      RAB3+K3*(6*RAB2*C-1))+PHIMC*(12*C2*K2*RAB3+16*C3*RAB3-K3*(6*
      RAB2*C-1)))/(32*EXP2*C6*RAB3)
0182      IF(LA(6)) GO TO 500
0183      R6= (-PI*ABX*(K*RTPI*EXP1*RAB*(PHIPC*EXP22+PHIMC)-PHIPC*RTPI*
      EXP1*EXP22*RTPI*EXP1*PHIMC-4*EXP2*RAB*RTC*EXP5M))/(4*EXP2*RTC
      *C2*RAB3)
0184      GO TO 500
0185      C7=C5*C
0186      RAB6=RAB3*PAR3
0187      RAB7=RAB5*RAB
0188      K5=K4*K
0189      K6=K5*K
0190      IF(RAE.LT.1.D-10) GO TO 309
0191      IF(ITYPE.NE.4) GO TO 302
0192      IF(INTC) GO TO 301
0193      RMAX1=DMIN(RMAX,1.D10)
0194      RMAX2=DMIN(RMAX,1.D1C*(1./3.))
0195      IF(.NOT.LA(1)) CALL NDCG32(RMIN,RMAX1,GSS,HM3,NGQ)
0196      IF(.NOT.LA(2)) CALL NDCG32(RMIN,RMAX2,GS6,HM6,NGQ)
0197      GO TO 302
0198      HDEN1=1.D8/STEPM
0199      HDEN2=(1.D8)*(1./3.)/STEPM
0200      HIN1=DMIN(HEXP,HDEN1)*2*(NAPP-1)
0201      HIN2=DMIN(HEXP,HDEN2)*2*(NAPP-1)
0202      IF(.NOT.LA(1)) CALL ITRCME(GSS,HIN1,1.D-8,NAPP,HM3,IERR,RMIN)
0203      IF(.NOT.LA(2)) CALL ITRCME(GS6,HIN2,1.D-8,NAPP,HM6,IERR,RMIN)
0204      CONTINUE
0205      FORMAT(1H,4HFM3=E15.6,5X,4HHM6=E15.6)
0206      C<P / R / P > INTEGRALS
0207      H423=HM6
0208      ABX=0.0D0
0209      EFX=0.0D0
0210      IF(ITYPE.NE.4) GO TO 310
0211      ABX=RAB
0212      IF(ICNTR.NE.JCNTR) EFX=R
0213      ABX2=ABX*ABX
0214      EFX2=EFX*EFX
0215      IF(ICNTR.NE.2) GO TO 311
0216      A=FXI
0217      R=FXJ
0218      GC TO 312
0219      A=FXI
0220      GC TO 312
0221      A=FXJ
0222      GC TO 312
0223      A=FXI
0224      GC TO 312
0225      A=FXJ
0226      GC TO 312
0227      A=FXI
0228      GC TO 312
0229      A=FXJ
0230      GC TO 312
0231      A=FXI
0232      GC TO 312
0233      A=FXJ
0234      GC TO 312
0235      A=FXI
0236      GC TO 312
0237      A=FXJ
0238      GC TO 312
0239      A=FXI
0240      GC TO 312
0241      A=FXJ
0242      GC TO 312
0243      A=FXI
0244      GC TO 312
0245      A=FXJ
0246      GC TO 312
0247      A=FXI
0248      GC TO 312
0249      A=FXJ
0250      GC TO 312
0251      A=FXI
0252      GC TO 312
0253      A=FXJ
0254      GC TO 312
0255      A=FXI
0256      GC TO 312
0257      A=FXJ
0258      GC TO 312
0259      A=FXI
0260      GC TO 312
0261      A=FXJ
0262      GC TO 312
0263      A=FXI
0264      GC TO 312
0265      A=FXJ
0266      GC TO 312
0267      A=FXI
0268      GC TO 312
0269      A=FXJ
0270      GC TO 312
0271      A=FXI
0272      GC TO 312
0273      A=FXJ
0274      GC TO 312
0275      A=FXI
0276      GC TO 312
0277      A=FXJ
0278      GC TO 312
0279      A=FXI
0280      GC TO 312
0281      A=FXJ
0282      GC TO 312
0283      A=FXI
0284      GC TO 312
0285      A=FXJ
0286      GC TO 312
0287      A=FXI
0288      GC TO 312
0289      A=FXJ
0290      GC TO 312
0291      A=FXI
0292      GC TO 312
0293      A=FXJ
0294      GC TO 312
0295      A=FXI
0296      GC TO 312
0297      A=FXJ
0298      GC TO 312
0299      A=FXI
0300      GC TO 312
0301      A=FXJ
0302      GC TO 312
0303      A=FXI
0304      GC TO 312
0305      A=FXJ
0306      GC TO 312
0307      A=FXI
0308      GC TO 312
0309      A=FXJ
0310      GC TO 312
0311      A=FXI
0312      GC TO 312
0313      A=FXJ
0314      GC TO 312
0315      A=FXI
0316      GC TO 312
0317      A=FXJ
0318      GC TO 312
0319      A=FXI
0320      GC TO 312
0321      A=FXJ
0322      GC TO 312
0323      A=FXI
0324      GC TO 312
0325      A=FXJ
0326      GC TO 312
0327      A=FXI
0328      GC TO 312
0329      A=FXJ
0330      GC TO 312
0331      A=FXI
0332      GC TO 312
0333      A=FXJ
0334      GC TO 312
0335      A=FXI
0336      GC TO 312
0337      A=FXJ
0338      GC TO 312
0339      A=FXI
0340      GC TO 312
0341      A=FXJ
0342      GC TO 312
0343      A=FXI
0344      GC TO 312
0345      A=FXJ
0346      GC TO 312
0347      A=FXI
0348      GC TO 312
0349      A=FXJ
0350      GC TO 312
0351      A=FXI
0352      GC TO 312
0353      A=FXJ
0354      GC TO 312
0355      A=FXI
0356      GC TO 312
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0249 RA= (PI*(2*(RAB3*RTI*RTPI*EXP1*(3*RAB*(PHIPC*EXP22+PHIMC)*ABX2*C-
    PHIPC*(2*(RAB3*ABX2+3*AB5)*C2+RAB3*(C2*EXP22-PHIMC*(2*(RAB3*
    ABX2+3*AB5)*C2+RAB3*(C2*EXP22-PHIMC*(2*(RAB3*ABX2+3*AB5)*C2+
    RTI*RTPI*EXP1*PHIMC*(C2+RAB3*(C2*EXP22-PHIMC*(2*(RAB3*ABX2+3*
    PHIPC*RTPI*EXP1*(4*(K2*RAE4*APX2-RAB2*ABX2+2*AB4)*C2-(2*ABX2
    *C+1)*RAB2-6*AB4*(C-3*ABX2)*K2+(4*ABX2*(C+1)*K3*RAE3+3*AB5*
    *K4*RAE2*ABX2-2*AB2*(C+6*ABX2)*C2-(2*ABX2*(C+1)*RTI*RTPI*
    PHIMC*(2*(RAB3*ABX2+3*AB5)*C2+RAB3*(C2*EXP22-PHIMC*(2*(RAB3*
    ABX2+3*AB5)*C2+RAB3*(C2*EXP22-PHIMC*(2*(RAB3*ABX2+3*AB5)*C2+
    -2*RAE2*(C+6*ABX2)*C2+RAB3*(C2*EXP22-PHIMC*(2*(RAB3*ABX2+3*
    K2*RAE3*(C+6*ABX2)*C2+RAB3*(C2*EXP22-PHIMC*(2*(RAB3*ABX2+3*
    IF(LA(5)) GO TO 323
    R5= (PI*(2*(RAB3*ABX2+3*AB5)*C2+RAB3*(C2*EXP22-PHIMC*(2*(RAB3*
    RAB2*ABX2-18*(C2*RAB4-12*(C3*RAE4*ABX2-16*(C3*RAE6+3*RAE2*(C-9*
    ABX2)*C2+RAB3*(C2*EXP22-PHIMC*(2*(RAB3*ABX2+3*AB5)*C2+RAB3*(
    *ABX2+RAB5)))-3*RAE*ABX2*(EXP1*RTI*RTPI*(PHIPC*EXP22+PHIMC)*
    G*K2*(C+K4)-4*EXP2*EXP5*(K3*(C)+EXP1*RTI*RTPI*(PHIPC*EXP22*(12*
    C2*(2*(K2*(RAE3*ABX2+RAE5)*K3*RAE4*ABX2)+8*(C3*RAE5*(K2*ABX2+5)
    +16*(C4*RAE7+6*(K2*PAB3*(C-K3*(RAE2-8*RAE4*(C-3*ABX2)+K4*RAE3*(6*
    ABX2*(C+1)*K5*RAE2*ABX2)+PHIMC*(12*(C2*(2*(K2*(RAB3*ABX2+RAB5)-
    K3*RAE4*ABX2)+8*(C3*RAE5*(K2*ABX2+5)+16*(C4*RAE7+6*(K2*RAE3*(C+K3
    *(RAE2-8*RAE4*(C-3*ABX2)+K4*RAE3*(6*ABX2*(C+1)-K5*RAE2*ABX2))-4
    *EXP2*EXP5*(K3*RAE3*(4*(C2*ABX2+C)))/(64*EXP2*(C7*RAE5)
    IF(LA(6)) GO TO 500
    R6= (PI*(K*RTI*EXP1*(3*RAE*ABX2-RAB3)*(PHIPC*EXP22+PHIMC)-
    PHIPC*RTPI*EXP1*(K2*RAE*ABX2-RAB2+2*RAE4*(C+3*ABX2)*EXP22+
    RTPI*EXP1*PHIMC*(K2*RAE*ABX2-RAB2+2*RAE4*(C+3*ABX2))-4*EXP2*
    RTI*(2*(ABX2*(C-1)*RAE3+3*RAE*ABX2)*EXP5*(C)))/(96*EXP2*(C3*
    RAB5)
    GC TO 500
    IF(.NOT.LA(1)) R1=4*PI/3*PI
    IF(.NOT.LA(2)) R2=4*PI/3*PI
    C DEF
    IF(LA(3)) GC TO 351
    R3= (-PI*(20*(K*RTI*(C-RTI*EXP1*PHI0C*(12*(C2+12*(K2*(C+K4))+2*RTI*
    K3))/(24*RTI*(C4)
    IF(LA(4)) GC TO 352
    R4= (-PI*(60*(K*RTI*(RTI*EXP1*PHI0C*(C2+(RTI*RTI*EXP1*PHI0C*(20
    *K3*(C+K5)-36*(C2*(K2-64*(C3-2*(K4*(C)))/(48*(C6)
    IF(LA(5)) GC TO 353
    R5= (-PI*(264*(K*(C3-RTI*EXP1*RTI*PHI0C*(180*(C2*(K2+120*(C3+30*(K4
    *C+K6)+2*(24*(C2*(K3+K5*(C)))/(96*(C7)
    IF(LA(6)) GC TO 500
    R6= (-PI*(6*(K*RTI*EXP1*PHI0C*(C+RTI*PHI0C-2*RTI*(K2+4
    *C)))/(12*RTI*(C3)
    RINT=R1
    RINTG(2)=R2
    RINTG(3)=R3
    RINTG(4)=R4
    RINTG(5)=R5
    RINTG(6)=R6
    FORMAT(1H ,2X,1H1,4X,2HFI/6(1H ,3X,E20.12/),1H ,SHRINT=E20.12)
    RETURN
    END

```

```

0001 REAL FUNCTION GS1*(R)
0002 IMPLICIT REAL*(A-H,O-Z)
0003 COMMON/INT/GAM,DK,RAB,DKG,ITYPE
0004 COMMON/PUT/PGTCK(15),IPCI
0005 DATA PEACH,DALGAR/ 5PEACH,9DALGARNO/
0006 IF(R.LT.1.D-10) GC TC 100
0007 R2=R*R
0008 R3=R2*R
0009
0010 C*** TAKE OUT GO TC 99 FOR PEACH'S CUTOFF
0011 C
0012 C*** PEACH'S CUTOFF FUNCTION ***
0013 C
0014 CUTE=DK*R
0015 CUT=1.DD-DEXP(-CUT)*(1.DD+CUT*(1.DD+CUT*.5DD))
0016 CUT=CUT*CUT
0017 PGTCK(10)=PEACH
0018 GC TO 99
0019
0020 CUTE=DK**6*R3**2
0021 PGTCK(10)=DALGAR
0022 IF(CUT.GT.1.D-10) CUT=1.DD-DEXP(-CUT)
0023 IF(RAB.LT.1.D-10) GO TO 110
0024 GS1=CUT*(DEXP(-GAM*(R-RAB)**2))
0025 U=-DEXP(-GAM*(R+RAB)**2))/(R3*2.)
0026 RETURN
0027
0028 110 IF(ITYPE.NE.1) GC TC 120
0029 GS1=CUT*DEXP(-GAM*R2)*2.*GAM/R2
0030 RETURN
0031
0032 100 GS1=0.DD
0033 RETURN
0034
0035 120 GS1=CUT*DEXP(-GAM*R2)
0036 C CHECK THIS EQU
0037 RETURN
0038 END

```

FORTRAN IV G LEVEL 21

GS2

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```

0001 REAL FUNCTION GS2*(R)
0002 I=1
0003 COMMON/INT/GAM,DK,RAB,DKQ,ITYPE
0004 COMMON/POT/POTCK(15),IPOT
0005 DATA PEACH,DALGAR/ 5FFPEACH,8FDALGARND/
0006 IF(P.LT.1.D-10) GC TO 100
0007 R2=R*R
0008 R4=R2*R2

C*** TAKE OUT GO TO 98 FOR PEACH'S CUTOFF
C GC TO 98
C*** PEACH'S CUTOFF FUNCTION ***
0009 CUT=DKQ*R
0010 CUT=1.D-DEXP(-CUT)*(1.D+CUT*(1.D+CUT*(.5D0+CUT/6.D0)))
0011 CUT=CUT*CUT
0012 POTCK(11)=PEACH
0013 GO TO 99
0014 CUT=DK**R**R**2
0015 POTCK(11)=DALGAR
0016 IF(CUT.GT.1.D-10) CUT=1.D-DEXP(-CUT)
0017 IF(RAB.LT.1.D-10) GC TO 110
0018 GS2=CUT*(DEXP(-GAM*(R-RAE)**2)-
UDEXP(-GAM*(R+RAB)**2))/(R4*R2.)
RETURN
0019 IF(ITYPE.NE.1) GC TO 120
0020 GS2=CUT*DEXP(-GAM*R2)*2.*GAM/R4
0021 RETURN
0022 GS2=0.D0
0023 RETURN
0024 GS2=CUT/R2*DEXP(-GAM*R2)
0025 C CHECK THIS EQU
RETURN
0026 END
0027

```

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G53

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```

0001 REAL FUNCTION GS3*8(R1
0002 IMPLICIT REAL*8(A-H,C-Z)
0003 COMMON/INT/GAM,DK,RAB,OKQ,ITYPE
0004 COMMON/FCT/PCTCK(15),JPCT
0005 DATA PEACH,DALGAR/ SHFEACH,8HDLGARNC/
0006 IF(R.LT.1.0-10.0R,RAB.LT.1.0-10) GO TO 100
0007 R2=R*R
C*** TAKE OUT GO TO 98 FOR PEACH'S CUTOFF
C
C*** PEACH'S CUTOFF FUNCTION ***
0008
0009 97 CUT=OK*R
0010 CUT=1.00-DEXP(-CUT)*(1.00+CUT*(1.00+CUT*.5D0))
0011 CUT=CUT*CUT
0012 PCTCK(12)=PEACH
0013 GO TO 99
0014 CUT=DK**6*D2**3
0015 PCTCK(12)=DALGAR
0016 IF(CUT.GT.1.0-10) CUT=1.00-DEXP(-CUT)
0017 GS3=CUT*(DEXP(-GAM*(R-RAB)**2)
0018 U +DEXP(-GAM*(R+RAE)**2))/(R2*2.)
0019 RETURN
0020 GS3=0.0D0
END

```


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GS4

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```

0001 REAL FUNCTION GS4*(R)
0002 IMPLICIT REAL*8(A-H,O-Z)
0003 COMMON/INT/GAM,DK,RAE,DKG,ITYPE
0004 COMMON/POI/POICK(15),IPOT
0005 DATA PEACH,GALGAR,SPFEACH,8*PCALGARND/
0006 IF(R,LT,1.0-10.0*OR,RAB,LT,1.0-10) GO TO 100
0007 R2=R**R
0008 R4=R2**R2
0009 C** TAKE OUT GO TO 98 FOR PEACH'S CUTOFF
0010 C GO TO 98
0011 C** PEACH'S CUTOFF FUNCTION ***
0012 97 CUT=DKQ*R
0013 CUT=1.00-DEXP(-CUT)*(1.00+CUT*(1.00+CUT*(.500+CUT/6.00)))
0014 CUT=CUT*CUT
0015 POICK(13)=PEACH
0016 98 GO TO 99
0017 CUT=DK**9*R4**2
0018 POICK(13)=DALGAR
0019 IF(CUT,GT,1.0-10) CUT=1.00-DEXP(-CUT)
0020 GS4=CUT*(DEXP(-GAM*(R-RAH)**2)
0021 U+DEXP(-GAM*(R+RAE)**2))/(R4**2.)
0022 RETURN
0023 GSA=0.000
0024 RETURN
0025 END

```

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G55

```

0001 REAL FUNCTION G55*(R)
0002 IMPLICIT REAL*8(A-H,C-Z)
0003 COMMON/INT/GAM,DK,RAB,DKQ,ITYPE
0004 CCYMON/FCT/PCTCK(15),IPCT
0005 DATA PEACH,DALGAR/ SHFEACH,8HMDALGARNC/
0006 IF(R,LT,1.D-10) GO TO 100
0007 R2=R*R
0008
0009 C*** TAKE CUT GO TO 98 FOR PEACH'S CUTOFF
0010 GC TO 98
0011 C*** PEACH'S CUTOFF FUNCTION ***
0012 97 CUT=DK*R
0013 CUT=1.D0-DEXP(-CUT)*(1.D0+CUT*(1.D0+CUT*.5D0))
0014 CUTE=CUT*CUT
0015 PCTCK(14)=PEACH
0016 GO TO 99
0017 98 CUT=DK**6*R2**3
0018 PCTCK(14)=DALGAR
0019 IF(CUT.GT.1.D-10) CUT=1.D0-DEXP(-CUT)
0020 IF(RAE,LT,1.D-10) GO TO 110
0021 G55=CUT*(DEXP(-GAM*(R-RAB)**2))/(R*2.)
0022 U -DEXP(-GAM*(R+RAB)**2))/(R*2.)
0023 RETURN
0024 110 G55=CUT*DEXP(-GAM*R2)*R2
0025 RETURN
0026 100 G55=0.000
0027 RRETURN
0028 END

```

```

0001 REAL FUNCTION GS6*(R)
0002 IMPLICIT REAL*8(A-H,C-Z)
0003 COMMON/INT/GAM,DK,RAB,DKQ,I TYPE
0004 COMMON/POT/POTCK(15),IPCT
0005 DATA PEACH,DALGAR/ SHFEACH,8+DALGARND/
0006 IF(R.LT.1.D-10) GO TO 100
0007 R2=R*R
0008 R3=R2*R
0009 C** TAKE OUT GO TO 98 FOR PEACH'S CUTOFF
0010 C
0011 C** PEACH'S CUTOFF FUNCTION ***
0012 97 CUT=DKQ*R
0013 CUT=1.D-DEXP(-CUT)*(1.D0+CUT*(1.D0+CUT*(.5D0+CUT/6.D0)))
0014 CUT=CUT*CUT
0015 POTCK(15)=PEACH
0016 GO TO 95
0017 98 CUT=DK**R2**4
0018 POTCK(15)=DALGAR
0019 IF(CUT.GT.1.D-10) CUT=1.D-DEXP(-CUT)
0020 IF(RAB.LT.1.D-10) GO TO 110
0021 GS6=CUT*(DEXP(-GAM*(R-RAB)**2)
0022 U -DEXP(-GAM*(R+RAB)**2))/(R3*2.)
0023 RETURN
0024 110 GS6=CLT*DEXP(-GAM*R2)
0025 RETURN
0026 100 GS6=0.D0
0027 RETURN
0028 END

```

APPENDIX D

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MAIN

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```

0001 IMPLICIT REAL*8(A-H,C-Z)
0002 LOGICAL RESTRT, LAI
0003 DIMENSION F(10), X(10), W(470)
0004 COMMON/FCN/INOUT,K,TIMLIM,DELM(10),LAI(6)
0005 COMMON/FIT/IS,IC,DD,FMIN,TINC,MAXFUN,IPRINT,DSTEP,
    * DMAX,ACC,W,RESTRT,MAXW
0006 EXTERNAL EPFIT
0007 READ(5,600)K,TIMLIM
0008 CALL STIME
0009 FORMAT(15,E10.5)
0010 READ(5,601)NVEXP,NVAR,MAXFUN,IPRINT,DSTEP,DMAX,ACC
0011 FORMAT(4I5,3E15.6)
0012 INOUT=1
0013 IF(K.LT.0) WRITE(6,620)
0014 IF(K.GE.0) WRITE(6,621)
0015 FORMAT(1H1,'FITTING PROGRAM -- INITIAL RUN'/)
0016 WRITE(6,622) TIMLIM,NVEXP,NVAR,MAXFUN,IPRINT,DSTEP,DMAX,ACC
0017 FORMAT(1H1,'TIMLIM=',F10.2/1H,'NVEXP=',F15.5X,'NVAR=',F15/
    * 1H,'MAXFUN=',F15.5X,'IPRINT=',F15/
    * 1H,'DSTEP=',F15.6,5X,'DMAX=',F15.6,5X,'ACC=',F15.6)
0018 RESTRT=K.GE.0
0019 IF(.NOT.RESTRT) GO TO 200
0020 READ(5,610) IS,IC,MAXW,DD,FMIN,TINC,(F(I),I=1,NVEXP)
0021 FORMAT(3I5,3E15.6/4E20.14))
0022 READ(5,611)(W(I),I=1,MAXW)
0023 FORMAT(4E20.14)
0024 CALL VA05AD(EPFIT,NVEXP,NVAR,F,X,DSTEP,DMAX,ACC,MAXFUN,
    * IPRINT,W)
0025 INOUT=-1
0026 CALL EPFIT(NVEXP,NVAR,F,X)
0027 STOP
0028 END
0029

```

FORTRAN IV C LEVEL

21

BLK DATA

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0001
0002
0003
0004
0005
0006

BLCK DATA
IMPLICIT REAL*8(A-H,C-Z)
REAL*4 TIME
COMMON/TEST/FEA,FEO,TIMEL(B)
DATA ERA,ER0/C.000000/
END

(200)

```

0001 SUBROUTINE EFFIT(NVEXP,NVAR,DIFF,PAR)
0002 IMPLICIT REAL*8(A-H,C-Z)
0003 REAL*4 TIME1,TIME2,TIME1(8),TIME2(8)
0004 LOGICAL RESTRT,RECALC(10),FCN8,LA(6),CLOSED
0005 LOGICAL NRC,LAR,LPA
0006 INTEGER*2 ISNX
0007 DIMENSION VEFF(10),DIFF(10),PAR(1),W(470)
0008 COMMON/QMAT/Q(1275,8),H(1275),HQ(1275)
0009 COMMON/FOT/POICK(15),IPOT
0010 COMMON/FCN/INCUT,K,TIMLIM,DELM(10),LAA(6)
0011 COMMON/EIT/IS,IC,DD,FMIN,TINC,MAXFUN,IPRINT,DSTEP,DMAX,ACC,
    *RESTRT,MAXW
0012 COMMON/SCLR/EXI,EXJ,ITYFF,JTYPE,ICNTR,JCNTR,R,CUT,CUT2,CUT3,
    *ALPHA,ALPHOB,AP(4),LA,RINTG(6),LAR
0013 COMMON/INCUT/VNHF(10),VAEN(10),VND(10),VNC(10),VNGD(10),VNOQ(10),
    *VNM1(10),VNM2(10),VNM3(10),VNM4(10),VEOD(10),VECG(10),VEM(6,10),
    *NFRST(50),NLAST(50),NCNTR(50),NTYPE(50),EX(100),CD(100),
    *PARVC(10),PARM(10),FARM(10),ZA,ZB,NVRST,NVXF,IVAR(10)
0014 COMMON/IN/ITILE(18),NBF,NORBA,NORBB,NSYM,DA(1275),DBA(1275),
    *DRAO(1275),
    *ALPHAQ,BETA1,FCNB(50),RVEXP(10),VEXP(10),ISNX(50),CLOSED,IPERT
0015 COMMON/TEST/EBA,EEQ,TIME1
0016 DATA IOUT,IIN/8,9/
0017 DATA PI2/1.57079632675485/
0018 XI2(X)=1.00-DEXP(-X)*(1.00+X*(1.00+500*X))
0019 XI3(X)=1.00-DEXP(-X)*(1.00+X*(1.00+X*(1.00+X/6.00)))
    C THIS PROGRAM CALCULATES A SUM OF DIFFERENCES BETWEEN A SET OF
    C "EXPERIMENTAL" POTENTIAL FCINTS AND THE VALUE CALCULATED USING
    C FIRST ORDER PERTURBATION THEORY FOR THE EFFECTIVE POTENTIAL.
    C IT IS DESIGNED TO BE CALLED BY TRUDGE AND TO BE USED TO FIT
    C THE POTENTIAL PARAMETERS
    C
    C INOUT .LT. 9 OUTPUT FOR RESTART
    C .EQ.0 ASSUMES ALL NEEDED INPUT PREVIOUSLY READ IN
    C .GT.0 READ INPUT AND CALCULATE FIRST VALUE
    C
    C PESTART .TRUE. RESTARTS CALCULATION USING PARAMETER VALUES
    C AND INTEGRALS FROM PREVIOUS RUN
    C
    C IOUT, IIN ARE FILES FOR RESTART OUTPUT FROM EFFPOT ONLY AND
    C FILES REQUIRED
    C 8 AND 9 (SEE ABOVE)
    C 1 AND 2
    C
    C SUBROUTINE POTHF (EXECUTED IF NOT RESTART) REQUIRES PLYATOM 1 JLK FILES FC
    C FILES FOR AB AND FOR AE WITH A HAVING ZERO NUCLEAR CHARGE FOR
    C ALL R VALUES TO BE FIT
    C
    C FILES FOR AE MUST BE CCNCATENATED ON TAPE1 AND THOSE FOR
    C AS A(0) ON TAPE2
    C 10 AND 11
    C
    C WHEN CALCULATING Q INTEGRALS, INTERMEDIATE RESULTS ARE
    C WRITTEN ON FILES 10 AND 11
    C
    C IPOT=1
    C NMAX=10
    C NVXP=NVEXP
    C
    C IF(INCUT.GE.0) GC TC 100
    C
    C 99 OUTPUT VALUES FOR RESTART
    C CALL CUTR(IOUT,NVAR,NMAX,DIFF,PAR)
    C STOP
    C
    C 100 NVRST=1
    C IF(INCUT.EQ.0) GC TC 200

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EPFIT

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```

C      READ INPJIT AND SET UP C1, C2
      CALL SETUP(NVAR,NMAX,PAR)
      IF(.NOT.RESTART) GO TO 170
C      READ IN RESTART PARAM
      CALL INR(IIN,IOUT,NVAR,NMAX,PAR)
C      CALCULATE NON-PARAM. DEPENDENT TERMS
      IF(NVRST.GT.NVEXP) GO TO 171
      CALL FOTMF(IOUT)
170  IF(.NOT.RESTRT) GO TO 204
171  IF(.NOT.RESTRT) AND CHECK IC SEE WHICH TERMS HAVE TO BE RECALCULATED
C      RESPT PARAMETERS AND CHECK IC
200  DO 190 I=1,NMAX
      IV=IVAR(I)
      IF(IV.EQ.0) GO TO 190
      PARM(I)=PARM0(I)+DATAN(PAR(IV))*DELM(I)
190  CONTINUE
      ALPHAC=PARM(10)
      ALPHAG=PARM(9)
      BETAI=PARM(8)
      DC 201 I=1,4
201  AP(I)=PARM(8-I)
      CUT2=PARM(3)
      CUT3=PARM(2)
      CUT=PARM(1)
      ALPHQE=ALPHAQ-6.00*BETAI
      DO 202 I=1,NMAX
202  RECALC(I)=.FALSE.
      IF(DABS(PARM(I))-PARM(I)).GT.1.D-10) RECALC(I)=.TRUE.
      WRITE(6,661)ALPHAQ,BETAI,CUT,CUT2,CUT3,AP
661  FORMAT(1H0,'EFFPUT EVALUATED WITH',/
      . 1H,'ALPHAQ=',E15.6,5X,'ALPHAG=',E15.6,5X,'BETAI=',E15.6/
      . 1H,'CUT=',E15.6,5X,'CUT2=',E15.6,5X,'CUT3=',E15.6/
      . 1H,'AP=',E15.6)
      CALL TTIME(TIME1)
      TIMER=TIME1-TIME1
      IF(TIMER.GE.TIME1) GC TO 320
      IF(RECALC(1)) GO TO 301
      IF(RECALC(2)) GO TO 304
      IF(RECALC(3)) GC TO 306
      IF(TIMER.GE.TIME1(9)) GO TO 320
      GC TO 319
301  IF(RECALC(2)) GO TO 302
      IF(RECALC(3)) GO TO 303
      IF(TIMER.GE.TIME1(2).AND.TIME1(2).GT.0.0) GO TO 320
      GC TO 319
302  IF(RECALC(3)) GO TO 319
      IF(TIMER.GE.TIME1(6).AND.TIME1(6).GT.0.0) GO TO 320
      GC TO 319
303  IF(TIMER.GE.TIME1(5).AND.TIME1(5).GT.0.0) GO TO 320
      GC TO 319
304  IF(RECALC(3)) GO TO 305
      IF(TIMER.GE.TIME1(4).AND.TIME1(4).GT.0.0) GO TO 320
      GC TO 319
305  IF(TIMER.GE.TIME1(7).AND.TIME1(7).GT.0.0) GO TO 320
      GC TO 319
306  IF(TIMER.GE.TIME1(3).AND.TIME1(3).GT.0.0) GO TO 320
319  WRITE(6,670) TIMER
670  FORMAT(1H0,'***** TIME LIMIT: SET UP RESTART *****'/
      . 1H,'F10.2)
      K=0

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EFFIT

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```

0079      GO TO 95
0080      C RFSET PARMO
0081      320 DC 203 I=1,10
0082      203 PARMO(I)=PARM(I)
0083      C CALCULATE NUCLEAR TERMS
0084      DO 220 N=1,NVEXP
0085      NRC=N.LT.NVRST .OR. INCUT.EQ.0
0086      R=RVEXP(N)
0087      IF(.NOT.RECALC(3).AND.NRC) GC TC 205
0088      VNQD(N)=X12(CUT2*R)/R**2
0089      VNQ(N)=VNQD(N)*VNGD(N)/2.C0
0090      205 IF(.NOT.RECALC(2).AND.NRC) GC TC 206
0091      VNQD(N)=X13(CUT3*R)/R**3
0092      VNQ(N)=VNQD(N)*VNGQ(N)/2.C0
0093      IF(.NOT.RECALC(1).AND.NRC) GO TO 220
0094      FXPR=DEXP(-CUT*R)
0095      VNMI(N)=EXPR
0096      VN2(N)=R*VNMI(N)
0097      VN3(N)=R*VN2(N)
0098      VN4(N)=EXPR/R
0099      220 CCNTINUE
0100      C *** DEBUG *****
0101      WRITE(6,660)(RVEXP(I),VND(I),VNQD(I),VNQ(I),VNGD(I),VNMI(I),
0102      VN2(I),VN3(I),VN4(I),I=1,NVEXP)
0103      660 FORMAT(1H0,2X,1HR,7X,3HVND,12X,4HVNQD,11X,3HNVG,12X,4HVNQG,
0104      11X,4HVNMI,11X,4HVN2,11X,4HVN3,11X,4HVN4/(1H ,F8.2,8E15.6))
0105      C *** DERUG *****
0106      C CALCULATE Q TERMS
0107      CALL FCTQ(RECALC)
0108      C SET UP RINT CALCULATION
0109      LAA(1)=.NOT.RECALC(3)
0110      LAA(2)=.NOT.RECALC(2)
0111      LAA(3)=.NOT.RECALC(1)
0112      DC 230 I=4,6
0113      230 LAA(I)=LAA(3)
0114      LAR=.TRUE.
0115      DC 235 I=1,6
0116      IF(.NOT.LAA(I)) GO TO 240
0117      CCNTINUE
0118      LAR=.FALSE.
0119      IF(NVRST.LE.NVEXP) GO TO 240
0120      GC TO 245
0121      C CALC R INTEGRALS
0122      240 CALL FCTR
0123      C CALC EFFECTIVE POTENTIALS AND THE SUM OF DIFFERENCES
0124      245 VPOT=C.000
0125      INOUT=0
0126      ZB2=ZB*ZB
0127      DO 300 N=1,NVEXP
0128      VNDA=-ZB2*ALPHAD*VND(N)
0129      VNQA=-ZB2*ALPHAQ*VNQ(N)
0130      VNMA1=ZB2*AP(1)*VNMI(N)
0131      VNMA2=ZB2*AP(2)*VNMI(N)
0132      VNMA3=ZB2*AP(3)*VNMI(N)
0133      VNMA4=ZB2*AP(4)*VNMI(N)
0134      VNQDA=ZB2*ALPHAD*VNQD(N)
0135      VNQQA=ZB2*ALPHAQ*VNQD(N)
0136      VEDA=-ALPHAD*VEQC(N)
0137      VEMA1=-ALPHAD*VEM(1,N)/2.D0

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```
0176 320 IF(IPERT.E2.0) RETURN
0177    FRAT=VEFF(1)+ERO
0178    WRITE(6,601) ERAT
0179    FORMAT(1H , 'TOTAL ENERGY FOR R=',E20.12)
0180    RETURN
0181    END
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OUTR

FORTRAN IV G LEVEL 21

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0001 SUBROUTINE OUTR(ICUT,NVAR,NMAX,F,PAR)
0002 IMPLICIT REAL*8(A-H,O-Z)
0003 LOGICAL RESIST,FCNB,CLOSED
0004 INTEGER*2 ISNX
0005 DIMENSION F(1),PAR(1)
0006 COMMON/INOUT/VNHF(10),VABN(10),VND(10),VNG(10),VNQD(10),VNQQ(10),
0007 VNM1(10),VNM2(10),VNM3(10),VNM4(10),VEQD(10),VECG(10),VEM(6,10),
0008 NFIRST(50),NLA(50),NCNTR(50),NTYPE(50),EX(100),CO(100),
0009 PARXO(10),PARM(10),PARMO(10),ZA,ZB,NVRST,NVEXP,IVAR(10)
0010 COMMON/FCN/INOUT,K,TIMLIM,DELIM(10)
0011 COMMON/FLY/IS,IC,CD,FMIN,TINC,MAXFJN,IPRINT,DSTEP,DMAX,ACC,
0012 A(470),RESTRT,MAXW
0013 COMMON/IN/ITITLE(18),ABF,NCRPA,NOR3B,NSYM,DA(1275),DBA(1275),
0014 DRAD(1275),
0015 ALPHAQ,BETA1,FCNB(50),RVEXP(10),VEXP(10),ISNX(50),CLOSED,IPERT
0016 COMMON/TEST/EBA,EP?
0017 WRITE(7,609)K,TIMLIM
0018 FCRMAT(15,510.5)
0019 WRITE(7,673)NVEXP,NVAR,MAXFJN,IPRINT,DSTEP,DMAX,ACC
0020 FCRMAT(415,3E15.6)
0021 WRITE(7,673)IS,IC,MAXW,CC,FMIN,TINC,(F(1),I=1,NVEXP)
0022 FCRMAT(315,3E15.6/(4E20.14))
0023 WRITE(7,671)(W(I),I=1,MAXW)
0024 FCRMAT(4E20.14)
0025 WRITE(10UT,600)IVAR,(PARM(I),PARMO(I),I=1,NMAX),
0026 (PAR(I),I=1,NVAR)
0027 FORMAT(1015/(2E20.12))
0028 WRITE(6,610)NVEXP,NVAR,IVAR,(PARM(I),PARMO(I),I=1,NMAX)
0029 FORMAT(1H,0,***** CUTOUT VALUES FOR RESTART *****/
0030 1H,6HNVEXP=,15,EX,5HNVAR=,15/
0031 1H,5HIVAR:,1015/
0032 1H,4X,4HPARM,16X,5HPARMC/(1H,2E20.12))
0033 WRITE(6,609)(PAR(I),I=1,NVAR)
0034 FORMAT(1H,4X,3HPAR/(1H,2E20.12))
0035 WRITE(10UT,601)EBA,EBO
0036 WRITE(10UT,600)NVEXP
0037 WRITE(10UT,601)(RVEXP(I),I=1,NVEXP)
0038 WRITE(10UT,601)(VNHF(I),I=1,NVEXP)
0039 WRITE(10UT,601)(VABN(I),I=1,NVEXP)
0040 WRITE(10UT,601)(VND(I),I=1,NVEXP)
0041 WRITE(10UT,601)(VNG(I),I=1,NVEXP)
0042 WRITE(10UT,601)(VNQD(I),I=1,NVEXP)
0043 WRITE(10UT,601)(VNQQ(I),I=1,NVEXP)
0044 WRITE(10UT,601)(VNM1(I),I=1,NVEXP)
0045 WRITE(10UT,601)(VNM2(I),I=1,NVEXP)
0046 WRITE(10UT,601)(VNM3(I),I=1,NVEXP)
0047 WRITE(10UT,601)(VNM4(I),I=1,NVEXP)
0048 WRITE(10UT,601)(VEQD(I),I=1,NVEXP)
0049 WRITE(10UT,601)(VECG(I),I=1,NVEXP)
0050 WRITE(10UT,601)(VEM(I,J),J=1,NVEXP),I=1,6)
0051 FCRMAT(4E20.12)
0052 WRITE(6,611)
0053 FORMAT(1H,0,***** RESTART OUTPUT COMPLETED ***** )
0054 RETURN
0055 END

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0044 DC 106 I=1,NBF
0045 VAL=H(I)*F
0046 DBA(1)=DBA(IJ)+VAL*H(J)
0047 IJ=IJ+1
0048 DBA(IJ)=DBA(IJ)+VAL*H(J)
0049 CONTINUE
0050 CONTINUE
0051 READ(5,600) ITITLE
0052 WRITE(6,623) ITITLE
0053 FORMAT(1H'UNDISTORTED ATOM E: ',1H,18A4)
0054 CLOSED=.TRUE.
0055 DO 120 K=1,NORRB
0056 READ(5,602) KX,SYM,NX,E,F,(H(I),I=1,NBF)
0057 WRITE(6,622) KX,SYM,NX,E,F,(H(I),I=1,NBF)
0058 IJ=0
0059 IF(F.LT.1.D0) CLOSED=.FALSE.
0060 DC 116 I=1,NBF
0061 VAL=H(I)*F
0062 DBA(1)=DBA(IJ)+VAL*H(J)
0063 IJ=IJ+1
0064 IF(.NOT.CLOSED) DBA(IJ)=DBA(IJ)+VAL*H(J)
0065 DBA(IJ)=DBA(IJ)+VAL*H(J)
0066 CONTINUE
0067 CONTINUE
0068 IF(IPERT.EQ.1) GO TO 122
0069 DC 121 I=1,NSYM
0070 DBA(1)=DBA(I)
0071 DEAO(1)=DBO(1)
0072 WRITE(6,662)
0073 FORMAT(1H0,'FUNCTION FOR DISTORTED ATOM B = UNDISTORTED FUNCTION')
0074 GC TO 123
0075 READ(5,600) ITITLE
0076 WRITE(6,670) ITITLE
0077 FORMAT(1H'FUNCTION FOR DISTORTED ATOM E: ',18A4)
0078 DO 300 K=1,NORRB
0079 READ(5,602) KX,SYM,NX,E,F,(H(I),I=1,NBF)
0080 WRITE(6,622) KX,SYM,NX,E,F,(H(I),I=1,NBF)
0081 IJ=0
0082 DC 306 I=1,NBF
0083 VAL=H(I)*F
0084 DBA(1)=DBA(IJ)+VAL*H(J)
0085 IJ=IJ+1
0086 IF(F.LT.1.D0) DBA(IJ)=DBA(IJ)+VAL*H(J)
0087 DBA(IJ)=DBA(IJ)+VAL*H(J)
0088 CONTINUE
0089 CONTINUE
C READ POTENTIAL PARAMETERS
123 READ(5,603) ALPHA,ALPHAQ,BETA1
READ(5,603) CUT,CUT2,CUT3
READ(5,603) AP
603 FORMAT(4D15,E)
WRITE(6,624) ALPHA,ALPHAQ,BETA1,CUT,CUT2,CUT3,AP
624 FORMAT(1H0/5X,'***** FEACH'S CUTOFF FUNCTIONS *****/
5X,'DIPOLE PARAMETER.....',D15.8/
5X,'QUADRUPOLE PARAMETER.....',D15.8/
5X,'BETA1.....',D15.8/
5X,'CUTOFF PARAMETERS.....',3D15.8/
5X,'MONOPOLE PARAMETERS.....',4D15.8/
READ(5,631)DELM

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0097 631 FORMAT(5E15.6)
0098 WRITE(6,632) DELM
0099 632 FORMAT(1H0,' LIMITS ON VARIATION OF PARM(I)'/
      (1H,5E15.6))
0100 READ(5,626) IVAR
0101 626 FORMAT(10I5)
0102 WRITE(6,627)
0103 627 FORMAT(1H,' PARAMETERS VARIED IN THIS RUN'/
      (1H,' ORDER',5X,'PARAMETER'))
0104 PARM(10)=ALPHA
0105 PARM(5)=ALPHA
0106 PARM(8)=BETA
0107 DO 115 I=1,4
0108 PARM(8-I)=AP(I)
0109 119 PARM(3)=CUT2
0110 PARM(2)=CUT3
0111 PARM(1)=CUT
0112 NV=0
0113 DO 130 I=1,10
0114 IV=IVAR(I)
0115 IF(IV.EQ.0) GO TO 130
0116 IF(DABS(DELM(I)).LT.1.0-10) GO TO 131
0117 NV=NV+1
0118 IF(I.EQ.10) GO TO 129
0119 I1=I+1
0120 DO 125 J=1,10
0121 IF(IV.EQ.IVAR(J)) GO TO 131
0122 CONTINUE
0123 125 WRITE(6,628) IV,FM(I)
0124 628 FORMAT(1H,5X,15.5X,A8)
0125 CONTINUE
0126 GO TO 132
0127 131 WRITE(6,630) IV,IVAR,DELM
0128 630 FORMAT(1H0,' ***** ERROR IN PARAMETER VARIATION ORDER *****'/
      (1H,' IV=',15/1H,' IVAR:',10I5/
      (1H,' DELM:',1H,5E15.6))
      STOP
0129 CC 118 I=1,10
0130 PAR(I)=0.000
0131 PARM(I)=PARM(I)
0132 DELM(I)=DELM(I)/PI2
0133 118 PARM(I)=0.000
0134 IF(NV.EQ.NVAR) GO TO 140
0135 WRITE(6,640) NV,NVAR
0136 640 FORMAT(1H0,' ***** ERROR *****'/
      (1H,' INCORRECT NUMBER OF PARAMETERS VARIED'/
      (1H,' NV=',15.5X,' SHOULD = NVAR=',15/))
      STOP
0138 C READ POTENTIAL POINTS TO BE FIT
0139 140 READ(5,604) (RVEXP(I),I=1,NVEXP)
0140 604 FORMAT(2D15.8)
0141 WRITE(6,625) (RVEXP(I),I=1,NVEXP)
0142 625 FORMAT(1H0,' POTENTIAL POINTS TO BE FIT'/
      (15X,1HR,16X,4HV(R))/(1X,D15.8,2X,D15.8))
0143 C DETERMINE WHICH BASIS FCNS USED FOR ATCM B
0144 I1=0
0145 DO 210 I=1,NDF
0146 210 I1=I+1
      FCNB(I)=.TRUE.

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0147 IF(DRA(II).EQ.0.0E0) FCNP(1)=.FALSE.
0148 RETURN
0149 END


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0001 SUBROUTINE POTHF(IOUT)
0002 IMPLICIT REAL*8(A-H,C-Z)
0003 LOGICAL FCNR,CLOSED
0004 INTEGER*2 IA,IR,IC,IO,IMU,IF,ISNX
0005 COMMON/INTS/NINTS,IA(500),IR(500),IC(500),IO(500),IMU(500),
0006 IF(500),V(500),VO(500)
0007 COMMON/INCUT/VNHF(10),VAFN(10),VND(10),VNO(10),VNOQ(10),VNOQ(10),
0008 VNM1(10),VNM2(10),VNM3(10),VNM4(10),VEQC(10),VEQC(10),VEM(6,10),
0009 NFIRST(50),NLAST(50),NCNTR(50),NTYPE(50),EX(100),CO(100),
0010 BARMC(10),PARM(10),FARM0(10),ZA,2B,NVRST,NVEXP,IVAR(10),
0011 COMMON/IN/TITLE(18),NBF,NORBA,NCRBB,NSYM,DA(1275),DRA(1275),
0012 CBAQ(1275),
0013 ALDHAQ,BETA1,FCNE(50),FVEXF(10),VEXP(10),ISNX(50),CLOSED,IPERT
0014 COMMON/QMAT/QB(1275),DBO(1275),DA1(1275),DA2(1275),H(1275),
0015 HC(1275),DKO(1275),DKAC(1275)
0016 COMMON/TEST/CBA,EB0
0017 DATA IJLK/4HIJLK/
0018
0019 C CALCULATE HARTREE-FOCK TERMS
0020 C DIVIDE DIAG DA,DB,ELEMENTS BY 2, CALC ISNX ARRAY, AND FORM
0021 C DENSITY MATRICES FOR ATOM A 2J-K POTENTIAL
0022
0023 IF(I)=0
0024 DO 129 I=1,NSYM
0025 IF(.NOT.CLOSED) DKO(I)=-CEC(I)
0026 DA1(I)=DA(I)*2.00
0027 CA2(I)=-DA(I)
0028 IF(I)=0
0029 DO 129 I=1,NBF
0030 ISNX(I)=11
0031 IF(I)=11
0032 DA(I)=DA(I)*0.500
0033 IF(.NOT.CLOSED) DBQ(I)=CEC(I)*0.500
0034 DBA(I)=DRA(I)*0.500
0035 IF(.NOT.CLOSED)CBAC(I)=DEAO(I)*0.500
0036 DR(I)=DB(I)*0.500
0037 C CALCULATE ELECTRONIC HF TERMS AND < B | ZA/RA + ZB/RB | B >
0038 VARN(N)=0.000
0039 VAR=0.000
0040 READ(1) ITITLE
0041 WRITE(6,626) ITITLE
0042 FCRMAT(5X,'FILE #1 TITLE =',18A4)
0043 IF(ITITLE(18).NE.IJLK) GO TO 121
0044 IF(N.NE.1) GO TO 125
0045 C READ BASIS SET INFORMATION AND OUTPUT FOR RESTART
0046 READ(1)II,(NFIRST(I),NLAST(I),NCNTR(I),NTYPE(I),I=1,II)
0047 IF(II.EQ.NBF) GO TO 122
0048 WRITE(6,627)
0049 FCRMAT(5X,'***** INPUT FILE ERROR *****')
0050 STOP
0051 WRITE(IOUT,600)II,(NFIRST(I),NLAST(I),NCNTR(I),NTYPE(I),I=1,II)
0052 FCRMAT(15/4I5)
0053 READ(1) II,(VAL,VAL,VAL,EX(I),CC(I),I=1,II),(V(I),I=1,II)
0054 WRITE(IOUT,601)II,(EX(I),CO(I),I=1,II),(V(I),I=1,II)
0055 FCRMAT(15/4E20,12)
0056 READ(1)II,X1,Y1,Z1,ZA,X2,Y2,Z2,ZB
0057 IF(II.NE.2) GO TO 121
0058 WRITE(IOUT,602) ZA,ZE
0059 FORMAT(2E20,12)
0060 WRITE(6,630)X1,Y1,Z1,ZA,X2,Y2,Z2,ZB

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0008      630  FCRMAT(IH0,10X,1HX,9X,1FY,9X,1HZ,9X,10HNUC CHARGE/
0049      * 1H,7HATOM A:.4F10.3/1H,7HATOM B:.4F10.3//)
0050      IF(Z2.NE.RVEXP(N)) GO TO 121
0051      GO TO 130
0052      READ(1)I1
0053      IF(I1.NE.NBF) GO TO 121
0054      READ(1)I1,X1,Y1,Z1,ZZA,X2,Y2,Z2,ZZB
0055      IF(I1.NE.2.OR.ZZA.NE.ZA.OR.ZZB.NE.ZB.CR.Z2.NE.RVEXP(N))
0056      * GO TO 121
0057      READ(1)I1
0058      READ(1)I1
0059      DC 124 I=1,NSYM
0060      H(I)=0.0D0
0061      I1I=2
0062      IF(IPERT.EQ.0) I1I=1
0063      DC 132 I=1,I1I
0064      READ(1)NINTS, LAST
0065      IF(LAST.EQ.0) GO TO 131
0066      READ(1)I1
0067      IF(IPERT.EQ.0) GO TO 133
0068      TB=0.0D0
0069      TBA=0.0D0
0070      READ(1)NINTS, LAST, IA, IB, IC, V
0071      IF(NINTS.EQ.0) GO TO 335
0072      DO 334 I=1, NINTS
0073      TB=TB+V(I)*DB(ISNX(IA(I))+IB(I))
0074      TBA=TBA+V(I)*DB(ISNX(IA(I))+IB(I))
0075      IF(LAST.EQ.0) GO TO 333
0076      WRITE(6,620) TB, TBA
0077      FORMAT(1H, 'KINETIC ENERGY TERMS: ',
0078      * 1H, 'TB=', E20.12/1H, 'TBA=', E20.12)
0079      READ(1)I1
0080      READ(1)NINTS, LAST, IA, IB, IC, V
0081      IF(NINTS.EQ.0) GO TO 135
0082      DO 134 I=1, NINTS
0083      H-(ISNX(IA(I))+IB(I))=V(I)
0084      IF(LAST.EQ.0) GO TO 133
0085      C CALCULATE ATOM A 2J-K POTENTIAL FROM UNIT 1 2E INTS AND ADD TO H
0086      READ(1)I1
0087      WRITE(6,680) I1
0088      FORMAT(1H, 'A9)
0089      CALL JKPT(H, DA1, DA2, ISNX, 1, HC, CKC, 'TRUE.')
0090      IF(IPERT.EQ.0) READ(1, END=136)
0091      IJ=0
0092      DO 137 I=1, NBF
0093      CC 137 J=1, I
0094      IJ=IJ+1
0095      VAB=VAB+H(IJ)*DBA(IJ)
0096      VABN(N)=4.*DO*VAB
0097      CONTINUE
0098      C ***
0099      WRITE(6,650)(VABN(I), I=1, NVEXP)
0100      FORMAT(1H, '2X,4HVABN/(1H, E20.12))
0101      C ***
0102      DERJG
0103      IF(IPERT.EQ.0) GO TO 360
0104      REWIND 1
0105      CC 331 I=1,6
0106      READ(1)

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0101 DO 312 I=1,3
0102 READ(1) NINTS, LAST
0103 IF (LAST.EQ.0) GO TO 336
0104 READ(1) I1
0105 I1=1
0106 DO 340 I=1, NSYM
0107 H(I)=0.000
0108 HC(I)=0.000
0109 DA2(I)=-DB(I)
0110 IF (I.NE.ISNX(I1+1)) GO TO 340
0111 I1=I1+1
0112 DA2(I)=2.*DA2(I)
0113 CA1(I)=-2.*DO*CA2(I)
0114 CALL JKPT(H, DA1, CA2, ISNX, I, HC, DKC, CLCSEC)
0115 VJKB=0.000
0116 IJ=0
0117 DO 337 I=1, NBF
0118 DC 337 J=1, I
0119 IJ=IJ+1
0120 VJKB=VJKB+H(IJ)*DB(IJ)+HO(IJ)*DBO(IJ)
0121 REWIND 1
0122 DO 341 I=1, 6
0123 READ(1)
0124 DC 342 I=1, 3
0125 READ(1) NINTS, LAST
0126 IF (LAST.EQ.0) GO TO 343
0127 READ(1) I1
0128 I1=1
0129 DC 350 I=1, NSYM
0130 H(I)=0.000
0131 HO(I)=0.000
0132 DA2(I)=-DBA(I)
0133 IF (.NOT.CLOSED) DKAO(I)=-DBAC(I)
0134 IF (I.NE.ISNX(I1+1)) GO TO 350
0135 I1=I1+1
0136 IF (.NOT.CLOSED) DKAO(I)=2.*DKAO(I)
0137 DA2(I)=2.*DO*DA2(I)
0138 DA1(I)=-2.*DO*DA2(I)
0139 CALL JKPT(H, DA1, CA2, ISNX, I, HO, DKAO, CLOSED)
0140 VJKB=0.000
0141 IJ=0
0142 DC 347 I=1, NBF
0143 DO 347 J=1, I
0144 IJ=IJ+1
0145 VJKB=VJKB+H(IJ)*DBA(IJ)+HO(IJ)*CRAC(IJ)
0146 WRITE(6, 621) VJKB, VJKB
0147 FCFORMAT(1H, 'CCULCMB TERMS: ',
0148 1H, 'VJKB=', E20.12, 'VJKB=', E20.12)
0149 EBA=4.00*TRA+2.00*VJKB+VABN(1)
0150 C CALCULATE NUCLEAR TERMS AND < B0 | ZB/RE | B0 >
0151 DO 160 N=NVRST, NVEXP
0152 VNH(N)=0.000
0153 VNF=0.000
0154 VAB=0.000
0155 READ(2) ITITLE
0156 WRITE(6, 631) ITITLE
0157 FORMAT(/5X, 'FILE #2 TITLE = ', 18A4)
0158 IF (ITITLE(18).NE.IJLK) GO TO 121
0159 READ(2) I1

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0158 IF(I1.NE.NBF) GO TO 121
0159 READ(2)
0160 READ(2) I1,X1,Y1,Z1,ZZA,X2,Y2,Z2,ZZE
0161 WRITE(6,671) I1,X1,Y1,Z1,ZZA,X2,Y2,Z2,ZZB
0162 FCRMAT(1H,*,I1=,15/(1H,4E15.6))
0163 IF(I1.NE.2.OR.Z2.NE.RVEXP(N)) GC TO 121
0164 READ(2) I1
0165 READ(2) I1
0166 DO 143 I=1,2
0167 READ(2) NINTS, LAST
0168 IF(LAST.EQ.0) GC TO 142
0169 READ(2) I1
0170 READ(2) NINTS, LAST, IA, IE, IC, V
0171 IF(NINTS.EQ.0) GO TO 146
0172 DC 145 I=1, NINTS
0173 VAR=VAB+V(I)*DB(ISNX(IA(I))+IE(I))
0174 VHF=VHF+V(I)*DA(ISNX(IA(I))+IB(I))
0175 IF(LAST.EQ.0) GC TC 144
0176 WRITE(6,672) VAB
0177 FORMAT(1H,*,VAB=,E15.6)
0178 VNH(N)=VHF*4.DO+ZA*ZE/RVEXP(N)
0179 IF(IPERT.EQ.0) VABN(N)=-VAB*4.DO+VABN(N)
0180 READ(2,END=160)
0181 IF(LAST.EQ.0) GO TO 147
0182 READ(2,END=160) NINTS, LAST
0183 IF(LAST.EQ.0) GO TO 147
0184 CONTINUE
0185 IF(IPERT.EQ.1) EBO=4.DO*TB+2.DO*VJB+4.DO*VAB
0186 WRITE(6,661)(VNH(I),VAEN(I),I=1,NVEXP)
0187 FCRMAT(1H,*,HARTREE-FOCK TERMS,/,
0188 1H,*,4X,*,4HVNH,16X,*,4HVAEN/(1H,2E20.12))
0189 RETURN
0189 END

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DEBUG***
DEBUG***

DEBUG***
DEBUG***

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0001 SUBROUTINE INR(IIN,ICUT,NVAR,NMAX,PAR)
0002 IMPLICIT REAL*8(A-H,C-Z)
0003 INTEGER*2 ISNX
0004 LOGICAL FCNR,RESTART,CLOSED
0005 DIMENSION RREST(10),PAR(1),IVRR(10)
0006 COMMON/FIT/IS,IC,CD,FMIN,TINC,MAXFUN,IPRINT,DSTEP,DMAX,ACC,
0007 *W(470),RESTART,MAXW
0008 COMMON/INTS/V(100)
0009 COMMON/INCU/VNHF(10),VARN(10),VND(10),VNQ(10),VNQD(10),VNQQ(10),
0010 *VN1(10),VN2(10),VN3(10),VN4(10),VEQD(10),VECG(10),VEM(6,10),
0011 *NFIRST(50),NLA(50),NCNTR(50),NTYPE(50),EX(100),CO(100),
0012 *PARMC(10),PARM(10),PARMO(10),ZA,ZB,NVRST,NVEXP,IVAR(10)
0013 COMMON/IN/TITLE(19),NDF,NORBA,NORBU,NSYM,DA(1275),DBA(1275),
0014 *DEAD(1275),
0015 *ALPHA0,BETA1,FCNB(50),RVEXP(10),VEXP(10),ISNX(50),CLOSED
0016 COMMON/TEST/EBA,EB0
0017 WRITE(6,660)
0018 FORMAT(1H0,***** RESTART PARAMETERS READ IN *****)
0019 READ(IIN,600) II,(NFIRST(I),NLA(I),NCNTR(I),NTYPE(I),I=1,II)
0020 WRITE(IOUT,600)II,(NFIRST(I),NLA(I),NCNTR(I),NTYPE(I),I=1,II)
0021 FCNTR(15/(415))
0022 READ(IIN,601)II,(EX(I),CC(I),I=1,II),(V(I),I=1,II)
0023 WRITE(IOUT,601)II,(EX(I),CC(I),I=1,II),(V(I),I=1,II)
0024 FCNTR(15/(4F20.12))
0025 READ(IIN,602) ZA,ZB
0026 WRITE(IOUT,602) ZA,ZB
0027 FCNTR(2E20.12)
0028 READ(IIN,610) IVRR,(PARM(I),PARMO(I),I=1,NMAX),
0029 * (PAR(I),I=1,NVAR)
0030 FORMAT(10I5/(2E20.12))
0031 READ(IIN,611) EBA,EB0
0032 READ(IIN,610)NVRST
0033 WRITE(6,605)ZA,ZB,NVRST
0034 FCNTR(1H, 'ZA=',E15.6, 'ZB=',E15.6/
0035 * 1H, 'NVRST=',I5)
0036 READ(IIN,611)(RREST(I),I=1,NVRST)
0037 READ(IIN,611)(VNHF(I),I=1,NVRST)
0038 READ(IIN,611)(VARN(I),I=1,NVRST)
0039 READ(IIN,611)(VND(I),I=1,NVRST)
0040 READ(IIN,611)(VNQ(I),I=1,NVRST)
0041 READ(IIN,611)(VNQD(I),I=1,NVRST)
0042 READ(IIN,611)(VEQD(I),I=1,NVRST)
0043 WRITE(6,606)VEQD
0044 FCNTR(1H, 'SE15.6)
0045 READ(IIN,611)(VN1(I),I=1,NVRST)
0046 READ(IIN,611)(VN2(I),I=1,NVRST)
0047 READ(IIN,611)(VN3(I),I=1,NVRST)
0048 READ(IIN,611)(VN4(I),I=1,NVRST)
0049 READ(IIN,611)(VEQD(I),I=1,NVRST)
0050 WRITE(6,606)VEQD
0051 READ(IIN,611)((VEM(I,J),J=1,NVRST),I=1,6)
0052 FORMAT(4E20.12)
0053 IF(NVRST.LT.NVEXP) GO TO 152
0054 II=0
0055 DO 100 I=1,NBF
0056 ISNX(I)=II
0057 II=II+I
0058 DA(II)=DA(II)+0.500

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```

0052 IF(.NOT.CLOSED) DBAO(II)=DBAC(II)*0.5D0
0053 CBA(II)=DBA(II)*0.5D0
0054 DO 150 I=1,NVRST
0055 IF(DABS(RVEXP(I))-RREST(I)).GT.1.D-10) GO TO 151
0056 CCNTINUE
0057 NVPST=NVPST+1
0058 DO 160 I=1,10
0059 IF(IVRR(I).NE.IVAR(I)) GC TO 170
0060 CONTINUE
0061 RETURN
0062 FMIN=-1.D0
0063 CC=0.000
0064 IS=4
0065 IC=0
0066 TINC=1.0D0
0067 DO 171 I=1,MAXN
0068 W(I)=0.000
0069 RETURN
0070 WRITE(6,661)(RREST(I),I=1,NVRST)
0071 FORMAT(1H0,'***** ERROR *****')
      . 1H 'ORDER OF RESTART DATA DOES NOT AGREE'
      . 1H 'EX.'RREST'/(1H ,E20.12)
      STOP
      END
0072
0073

```

```

0001 SUBROUTINE PCTR
0002 IMPLICIT REAL*8(A-H,O-Z)
0003 LOGICAL FCNB,LA,LAR,LPA
0004 INTEGER*2 ISNX
0005 DIMENSION VALR(6)
0006 COMMON/SCMR/RI(6,1275)
0007 COMMON/SCLR/EXI,EXJ,I TYPE,JTYPE,ICNTR,JCNTR,R,CUT,C 2,CUT3,
0008 ALPHA,ALPHAB,AP(4),LA(6),RINTG(6),LAR
0009 COMMON/INOUT/VNHF(10),VAEN(10),VNC(10),VNCQ(10),VNCQ(10),
0010 VNM1(10),VNM2(10),VNM3(10),VNM4(10),VEQ(10),VFCQ(10),VEM(6,10),
0011 NFRST(50),NLAST(50),NCNTR(50),NTYPE(50),FX(100),CD(100),
0012 PARMQ(10),PARM(10),PARMC(10),ZA,ZB,NVRST,NVFXP,IVAR(10),
0013 COMMON/IN/ITITLE(18),ABF,NOREA,NORBB,NSYM,DA(1275),DBA(1275),
0014 DBAQ(1275),
0015 ALPHAQ,BETA1,FCNB(50),RVEXP(10),VFXP(10),ISNX(50)
0016 COMMON/FCN/INOUT,K,TIMLIM,DELM(10),LAA(6)
0017 C INITIALIZE R
0018 CC 100 J=1,NSYM
0019 DC 100 I=1,6
0020 RI(I,J)=0.0D0
0021 C CALCULATE NEEDED NEW R INTEGRALS
0022 DO 400 N=1,NVEXP
0023 IF(N-GE-NVRST) GO TO 102
0024 IF(LAR) GC TC 105
0025 GO TO 400
0026 IF(INCJT.EQ.0) GO TO 101
0027 DC 103 I=1,6
0028 LA(I)=FALSE.
0029 GO TO 110
0030 DC 106 I=1,6
0031 LA(I)=LAA(I)
0032 R=RVEXP(N)
0033 IJ=0
0034 DC 350 I=1,NRF
0035 IF(ST=NFIRST(I))
0036 ILST=NLAST(I)
0037 I TYPE=NTYPE(I)
0038 ICNTR=NCNTR(I)
0039 DN 349 J=1,I
0040 IJ=IJ+1
0041 IF(.NOT.FCNB(I).OR..NCT.FCNB(J)) GO TC 349
0042 JIST=NFIRST(J)
0043 JLST=NLAST(J)
0044 JTYPE=NTYPE(J)
0045 JCNTR=NCNTR(J)
0046 DO 310 IR=1,6
0047 VALR(IR)=0.0D0
0048 DC 346 II=IIST,ILST
0049 EXI=EX(II)
0050 TEMPE=CO(II)
0051 DC 346 JJ=JIST,JLST
0052 EXJ=EX(JJ)
0053 TCO=TEMP*CO(JJ)
0054 VALR(I)=VALR(I)+TCO*RINT(ICUM)
0055 DO 345 IR=2,6
0056 VALR(IR)=VALR(IR)+TCO*RINTG(IR)
0057 CONTINUE
0058 DC 348 IR=1,6
0059 IF(LA(IR)) GO TO 348
0060

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0052 RI(IP,IJ)=VALR(IR)
0053 CONTINUE
0054 CONTINUE
0055 CONTINUE
0056 DO 355 IR=1,6
0057 VALR(IP)=0.000
0058 IJ=0
0059 DO 360 I=1,NRF
0060 DC 360 J=1,I
0061 IJ=IJ+1
0062 DO 358 IR=1,6
0063 VALR(IR)=VALR(IR)+RI(IR,IJ)*CBA(IJ)
0064 CONTINUE
0065 DC 361 IR=1,6
0066 IF(LA(IR)) GC TC 361
0067 VEM(IR,N)=VALR(IR)*4.00
0068 CONTINUE
0069 CONTINUE
0070 WRITE(6,601)((VEM(I,J),I=1,6),J=1,NVE*XP)
0071 FCRMAT(1H'.3HVEW/11H'.6E15.6)
0072 RETURN
0073 END

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0001 SUBROUTINE PUTQ(RECALC)
0002 IMPLICIT REAL*8(A-F,C-Z)
0003 LOGICAL RFALC(10),FCNB,LA,CLOSED
0004 INTEGER*2 IA,IB,IC,IC,IMU,IF,ISNX,JV(4),ISET(14),IVAL
0005 DIMENSION DB2(1275),HG(1275),HQC(1275),DRC2(1275)
0006 COMMON/OMAT/G(1275,8),H(1275),PO(1275)
0007 COMMON/INTS/INTS,LAST,IA(500),IB(500),IC(500),IMU(500),
    * IF(500),V(500),VG(500)
0008 COMMON/SLR/EXI,EXJ,IJTYPE,IJTYPE,JCNT,R,CUT,CUT2,CUT3,
    * ALPHA,ALPHQB,AP(4),LA(6),RINTG(6)
0009 COMMON/INOUT/VNHF(10),VAEN(10),VND(10),VND(10),VND(10),VND(10),VND(10),
    * VN4(10),VN2(10),VN3(10),VN4(10),VEQC(10),VEQC(10),VEQC(10),VEQC(10),
    * NFRST(50),NLAST(50),NCNTR(50),NTYPE(50),EX(100),CO(100),
    * PARM(10),PARM(10),PARM(10),ZA,ZB,NVRST,NVEXP,IVAR(10)
0010 COMMON/IN/ITITLE(18),NDF,NORBA,NCRBB,NSYM,DA(1275),DBA(1275),
    * DEAD(1275)
0011 ALPHA,ALPHQB,AP(4),VAEN(10),VND(10),VND(10),VND(10),VND(10),VND(10),
0012 EQUIVALENCE (VAL,JV),(IVAL,JV(4))
0013 DATA ISET/9,6,4,1,12,7,5,3,14,8,11,2,13,10/
    * ZERC/1,0-14/
C INITIALIZE Q AND SET UP C CALC
    NI=1
0014 IF(RECALC(3)) GO TO 212
0015 IF(RECALC(2)) GO TO 214
0016 GO TO 301
0017
212 KI=1
0018 KI=1
0019 KF=3
0020 IF(RECALC(2)) GO TO 215
0021 GO TO 216
214 KI=4
0022 KI=4
215 KF=8
0023 KF=8
216 DO 217 K=1,9
0024 DO 217 I=1,NSYM
0025 Q(I,K)=0.000
0026
C SET UP DP2
    CC 204 I=1,NSYM
0027 IF(.NCT.CLOSED) DE02(1)=-DEAC(1)
0028 DB2(1)=-DBA(1)
0029 I=0
0030 DO 205 I=1,NBF
0031 IF(I=1)
0032 IF(.NCT.CLOSED) DE02(11)=2.D0*DE02(11)
0033 DB2(11)=DB2(11)+DB2(11)
0034 CC 300 N=1,NVEX
0035 IF(N.LT.NVRST) GO TO 206
0036 KI=1
0037 KF=8
0038 R=RVEXP(N)
0039 IJ=0
0040
C CALCULATE NEEDED NEW Q INTS
    DO 230 I=1,NBF
0041 IJ=NFIRST(I)
0042 IJ=NLAST(I)
0043 IJ=INTYPE(I)
0044 IJ=NCNTR(I)
0045 DO 225 J=1,I
0046 IJ=IJ+1
0047 IF(.NCT.FCNB(I).OR..NCT.FCNB(J)) GO TO 225
0048

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0040 J1ST=FIRST(J)
0041 J1ST=LAST(J)
0042 JTYPE=TYPE(J)
0043 JCNTR=CNTR(J)
0044 DO 220 K=K1,KF
0045 VAL=0.0D0
0046 DO 215 II=I1ST,I1ST
0047 TEMP=CN(II)
0048 EXI=EX(II)
0049 DO 218 JJ=J1ST,J1ST
0050 EXJ=FX(JJ)
0051 VAL=VAL+TEMP*CO(JJ)*OINT(K)
0052 CONTINUE
0053 G(IJ,K)=VAL
0054 CONTINUE
0055 C***** DEBUG
0056 WRITE(6,605)((O(I,J),J=1,2),I=1,NSYM)
0057 605 FORMAT(1H,0 INTS'/(1H,RE15.6))
0058 C***** DEBUG
0059 IJ=0
0060 VAR=0.0D0
0061 VAR4=C.0D0
0062 DO 235 I=1,NRF
0063 DO 236 J=1,I
0064 IJ=IJ+1
0065 VAB=VAB+Q(IJ,I)*DBA(IJ)
0066 VAB4=VAB4+Q(IJ,4)*DBA(IJ)
0067 IF(KI.EQ.1) VNOC(N)=VNOC(N)*VAB4*.D0
0068 IF(KF.EQ.8) VNOC(N)=VNOC(N)*VAB4*.D0
0069 C***** DEBUG
0070 WRITE(6,610)VAB,VAB4
0071 610 FORMAT(1H,0 INT: VAB=, E15.6, VAB4=, E15.6)
0072 C***** DEBUG
0073 NINTS=0
0074 LAST=C
0075 IJ=0
0076 C FORM 2 EL 0 INTS
0077 DO 290 I=1,NRF
0078 LEQJ=0
0079 LSTOP=I-1
0080 DO 275 J=1,I
0081 IJ=IJ+1
0082 IF(I.NE.J) GC TO 236
0083 LSTOP=I
0084 LEQJ=2
0085 KSTOP=I
0086 DO 237 K=1,IJ
0087 HQ(K)=0.0D0
0088 IF(KI.NE.1) GC TO 242
0089 DO 240 K=1,3
0090 DC 239 KL=1,IJ
0091 H(KL)=H(KL)+G(KL,K)*O(IJ,K)
0092 CONTINUE
0093 IF(KF.NE.3) GO TO 243
0094 DO 241 KL=1,IJ
0095 HQ(KL)=HQ(KL)+G(KL,K)*O(IJ,K)
0096 CONTINUE
0097 IF(KF.NE.3) GO TO 243
0098 DO 241 KL=1,IJ
0099 HQ(KL)=HQ(KL)+G(KL,K)*O(IJ,K)
0100 CONTINUE
0101 IF(KF.NE.3) GO TO 243
0102 DO 241 KL=1,IJ
0103 HQ(KL)=HQ(KL)+G(KL,K)*O(IJ,K)

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0152 DC 231,1=1,NSYM
0153 H(1)=0.000
0154 HQ(1)=0.000
0155 HC(1)=0.000
0156 HJ(1)=0.000
0157 CFA(1)=-2.00+CB2(1)
0158 REWIND 10
0159 REWIND 11
0160
0161 IF (K1.EQ.1) CALL JKPCCT(P,CEA,CB2,ISNX,10,H0,DB02,
* .CLOSED)
IF (KF.EQ.8) CALL JKPCCT(HQ,DBA,DB2,ISNX,11,H00,DB02
* .CLOSED)
C***** DEBUG
0162 WRITE(6,607)(HQ(1),I=1,NSYM)
0163 FORMAT(1H, 'HQ',/(1H, 6E15.6))
C***** DEBUG
0164 REWIND 10
0165 REWIND 11
C CHANGE DB BACK
0166 DO 282 I=1,NSYM
0167 DBA(I)=DBA(I)/2.00
0168 I1=0
0169 DO 283 I=1,N0F
0170 I1=I1+1
0171 DBA(I1)=DBA(I1)/2.00
C CALC C < B B | 2J0-K0 | B B >
VAR=0.000
VAB4=C.000
VJ=0
0172 DO 285 I=1,NBF
0173 DO 286 J=1,I
0174 VAB=VAB+H(IJ)*DBA(IJ)+HC(IJ)*CEAC(IJ)
0175 VAB4=VAB4+HQ(IJ)*DBA(IJ)+HQQ(IJ)*DBAO(IJ)
0176 IF (K1.EQ.1) VEQD(N)=VAB+2.C0
0177 IF (KF.EQ.8) VEQD(N)=VAB4+2.00
C***** DEBUG
0178 WRITE(6,610)VAB,VAB4
C***** DEBUG
0179 CONTINUE
0180
0181 WRITE(6,601)(VNQD(I),VNQQ(I),VEQD(I),VEQQ(I),I=1,NVEXP)
0182 FORMAT(1H, 'Q INTEGRAL TERMS',/
* 1H, 4X, 4HVNQC,16X, 4HVNCC,16X, 4HVEQD,16X, 4HVEQQ/(1H, 4E20.12))
0183 RETURN
0184 IF (NVERST.GT.NVEXP)OR.INCUT.EQ.0) RETURN
0185 NI=NVRSI
0186 GO TO 210
0187
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0189
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0200

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0001      SUBROUTINE MBIIAD(M,N,A,IA,W)
0002      IMPLICIT REAL*8(A-P,O-Z)
0003      DIMENSION A(IA,1),W(1)
0004      PARTITION THE WORKING SPACE ARRAY W
0005      THE FIRST PARTITION FCLOS THE FIRST COMPONENTS OF THE VECTORS OF
0006      THE ELEMENTARY TRANSFORMATIONS
0007      N*W=M
0008      THE SECOND PARTITION RECORDS ROW INTERCHANGES
0009      N*W=M+M
0010      THE THIRD PARTITION RECORDS COLUMN INTERCHANGES
0011      SET THE INITIAL RECORDS OF ROW AND COLUMN INTERCHANGES
0012      DO 1 I=1,M
0013      W(NRW+I)=0.500+DFLOAT(I)
0014      DO 2 I=1,N
0015      W(NCW+I)=0.500+DFLOAT(I)
0016      *KK: COUNTS THE SEPARATE ELEMENTARY TRANSFORMATIONS
0017      KK=1
0018      FIND LARGEST ROW AND MAKE ROW INTERCHANGES
0019      DO 4 I=KK,M
0020      SUM=0.0D0
0021      DO 5 J=KK,N
0022      SUM=SUM+A(I,J)**2
0023      IF (RMAX-SUM) 6,4,4
0024      IF (IR-IR) 7,7,8
0025      W(NRW+KK)=W(NRW+IR)
0026      W(NCW+IR)=SUM
0027      DO 9 J=1,N
0028      SUM=A(KK,J)
0029      A(KK,J)=A(IR,J)
0030      A(IR,J)=SUM
0031      CCNTINUE
0032      FIND LARGEST ELEMENT OF PIVOTAL ROW, AND MAKE COLUMN INTERCHANGES
0033      DO 10 J=KK,N
0034      SUM=0.0D0
0035      SUM=SUM+A(KK,J)**2
0036      IF (RMAX-DABS(A(KK,J))) 11,10,10
0037      IF (RMAX=DABS(A(KK,J)))
0038      IR=J
0039      CCNTINUE
0040      IF (IR=KK) 12,12,13
0041      RMAX=W(NCW+KK)
0042      W(NCW+KK)=W(NCW+IR)
0043      W(NCW+IR)=RMAX
0044      DO 14 I=1,M
0045      RMAX=A(I,KK)
0046      A(I,KK)=A(I,IR)
0047      A(I,IR)=RMAX
0048      CCNTINUE
0049      REPLACE THE PIVOTAL ROW BY THE VECTOR OF THE TRANSFORMATION

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0100      CC 44 I=K,P,M
0101      SUM=SUM-A(I,KK)*W(I)
0102      A(I,KK)=W(I)
0103      44 CONTINUE
0104      A(KK,KK)=SUM/A(KK,KK)
0105      GO TO 36
0106      C
0107      RESTORE THE ROW INTERCHANGES
0108      37 DO 45 I=1,M
0109      46 IR=IDINT(W(NRW+I))
0110      IF (I-IR) 47,45,45
0111      47 SUM=W(NRW+I)
0112      W(NRW+I)=W(NRW+IR)
0113      W(NRW+IR)=SUM
0114      DO 48 J=1,N
0115      SUM=A(I,J)
0116      A(I,J)=A(IR,J)
0117      A(IR,J)=SUM
0118      48 CONTINUE
0119      GO TO 46
0120      C
0121      RESTORE THE COLUMN INTERCHANGES
0122      DO 49 J=1,N
0123      IR=IDINT(W(NCW+J))
0124      IF (J-IR) 51,49,49
0125      51 SUM=W(NCW+J)
0126      W(NCW+J)=W(NCW+IR)
0127      W(NCW+IR)=SUM
0128      DO 52 I=1,M
0129      SUM=A(I,J)
0130      A(I,J)=A(I,IR)
0131      A(I,IR)=SUM
0132      52 CONTINUE
0133      GO TO 50
0134      49 CONTINUE
0135      RETURN
0136      END

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0001 SUBROUTINE VA05AC(CALFUN,W,N,F,X,DSTEP,DMAX,ACC,MAXFUN,IPRINT,M)
0002 C***** 10/09/74 LAST LIBRARY UPDATE
0003 C
0004 C LOGICAL RESTRT
0005 C NOTE THAT THE INSTRUCTION CALLING SUBROUTINE 'MB11A',
0006 C CN LINE NUMBER '138', IS NOT STANDARD FORTRAN
0007 C DIMENSION F(1),X(1),W(1)
0008 C COMMON/FIT/IS,IC,DD,FMIN,TINC,EXX(474),RESTRT,MAXM
0009 C SET VARIOUS PARAMETERS
0010 C MAXC=C
0011 C *MAXC COUNTS THE NUMBER OF CALLS OF CALFUN
0012 C NPAR=M+N
0013 C NTEN=2
0014 C NTEST=0
0015 C *NT AND *NTEST CAUSE AN ERROR RETURN IF F(X) DOES NOT DECREASE
0016 C DTEST=FLOAT(N+N)-C.5
0017 C *DTEST IS USED IN A TEST TO MAINTAIN LINEAR INDEPENDENCE
0018 C PARTITION THE WORKING SPACE ARRAY W
0019 C THE FIRST PARTITION HOLDS THE JACOBIAN APPROXIMATION
0020 C ANI=M*N
0021 C THE NEXT PARTITION HOLDS THE GENERALIZED INVERSE
0022 C NWX=NWI+M*N
0023 C THE NEXT PARTITION HOLDS THE BEST VECTOR X
0024 C NWF=NWX+N
0025 C THE NEXT PARTITION HOLDS THE BEST VECTOR F
0026 C NWC=NWF+M
0027 C THE NEXT PARTITION HOLDS THE COUNTS OF THE INDEPENDENT DIRECTIONS
0028 C NWD=NWC+N
0029 C THE NEXT PARTITION HOLDS THE INDEPENDENT DIRECTIONS
0030 C NWK=NWD+N*N
0031 C THE REMAINDER OF M IS USED FOR SCRATCH VECTORS
0032 C NNV=NWK+N
0033 C NNU=NNV+M
0034 C MAXW=2*(N*(M+N)+M)+5*N
0035 C USUALLY 'FMIN' IS THE LEAST CALCULATED VALUE OF F(X)
0036 C USUALLY 'DD' IS THE SQUARE OF THE CURRENT STEP LENGTH
0037 C DSS=DSTEP*DSTEP
0038 C DM=DVAX*DMAX
0039 C PARM=DSQRT(ACC)/DMAX
0040 C *PARM IS THE LEAST VALUE OF THE MARQUARDT PARAMETER
0041 C *PAR=10.0D0*DM
0042 C *DPA AND 'NTPAR' ARE USED TO REGULATE THE MARQUARDT PARAMETER
0043 C *IS CONTROLS A GOTO STATEMENT FOLLOWING A CALL OF CALFUN
0044 C *TINC IS USED IN THE CRITERION TO INCREASE THE STEP LENGTH
0045 C START A NEW PAGE FOR PRINTING
0046 C IF(RESTRT) GOTO 200
0047 C FMIN=-1.0D0
0048 C DD=0.0D0
0049 C IS=4
0050 C IC=0
0051 C TINC=1.0D0
0052 C IF (IPRINT) 1,3,1
0053 C
0054 C 200 1 PRINT 2
0055 C 2 FORMAT (I1,4X,'THE FOLLOWING OUTPUT IS PROVIDED BY SUBROUTINE',
0056 C 1, VA05AC,/)
0057 C IFC=0
0058 C GO TO 3
0059 C TEST WHETHER THERE HAVE BEEN MAXFUN CALLS OF CALFUN

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0076      4 IF (MAXFUN-MAXC) 5,5,2
0077      5 IF (IPRINT) 139,140,139
0078      140 IPRINT=2
0079      GC TO 19
0080      139 PRINT 6,MAXC
0081      6 FCFORMAT (//5X,'ERROR RETURN FROM VA05A BECAUSE THERE HAVE BEEN',
0082      115,' CALLS OF CALFUN')
0083      GO TO 7
0084      C
0085      CALL THE SUBROUTINE CALFUN
0086      3 MAXC=MAXC+1
0087      CALL CALFUN (M,N,F,X)
0088      C
0089      CALCULATE THE SUM OF SQUARES
0090      FSQ=0.000
0091      DO 8 I=1,M
0092      FSQ=FSQ+F(I)*F(I)
0093      8 CONTINUE
0094      C
0095      TEST FOR ACC
0096      IF(FSQ-ACC) 180,180,181
0097      180 WRITE(6,780)
0098      780 FCFORMAT(//1H,'FSC .LT. ACC//')
0099      GO TO 7
0100      C
0101      TEST FOR ERROR RETURN BECAUSE F(X) DOES NOT DECREASE
0102      181 GO TO (9,10,9,10),I5
0103      9 IF (FSQ-FMIN) 11,12,12
0104      12 IF (DC-DSS) 13,13,10
0105      13 NTEST=NTEST-1
0106      IF (NTEST) 14,14,10
0107      14 IF (IPRINT) 15,17,15
0108      17 IPRINT=1
0109      GC TO 19
0110      15 PRINT 16
0111      16 FORMAT (//5X,'ERROR RETURN FROM VA05A BECAUSE F(X) NO LONGER',
0112      1, 'DECREASES',//5X,'THIS MAY BE DUE TO THE VALUES OF DSTEP',
0113      2, 'AND ACC, OR TO LOSS OF RANK IN THE JACCOBIAN MATRIX')
0114      C
0115      PROVIDE PRINTING OF FINAL SOLUTION IF REQUESTED
0116      7 IF (IPRINT) 18,19,18
0117      18 PRINT 20,MAXC
0118      20 FCFORMAT (//5X,'THE FINAL SOLUTION CALCULATED BY VA05A REQUIRED',
0119      115,' CALLS OF CALFUN, AND IS')
0120      PRINT 21,(I,W(NWX+1),I=1,N)
0121      21 FORMAT (//4X,'I',7X,'X(I)',10X,'I',7X,'X(I)',
0122      110X,'I',7X,'X(I)',10X,'I',7X,'X(I)',//5(15,D17.8))
0123      PRINT 22,(I,W(NWF+1),I=1,M)
0124      22 FORMAT (//4X,'I',7X,'F(I)',10X,'I',7X,'F(I)',
0125      110X,'I',7X,'F(I)',10X,'I',7X,'F(I)',//5(15,D17.8))
0126      PRINT 23,FMIN
0127      23 FORMAT (//5X,'THE SUM OF SQUARES IS',D17.8)
0128      C
0129      RESTORE THE BEST VALUES OF X AND F
0130      DO 135 I=1,N
0131      X(I)=W(NWX+1)
0132      DO 136 I=1,M
0133      F(I)=W(NWF+1)
0134      135 CCNTINUE
0135      136 CONTINUE
0136      RETURN
0137      11 NTEST=NT
0138      C
0139      PROVIDE ORDINARY PRINTING IF REQUESTED
0140      10 IF (IAES(IPRINT)-1) 35,36,4C
0141      38 PRINT 41,MAXC

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0082 41 FORMAT (//5X,'AT THE',IS,'TH CALL OF CALFUN WE HAVE')
0083 42 PRINT 21,(I,X(I),I=1,N)
0084 PRINT 23,FSC
0085 IF (I PRINT) 39,39,142
0086 142 PRINT 22,(I,F(I),I=1,M)
0087 GO TO 39
0088 40 IPC=IPC-1
0089 IF (IPC) 43,43,39
0090 43 PRINT 44,MAXC
0091 44 FORMAT (//5X,'THE BEST ESTIMATE AFTER',IS,' CALLS OF CALFUN IS')
0092 IPC=IABS(IPRINT)
0093 IF (FSC-FMIN) 42,45,45
0094 45 IF (FMIN) 42,46,46
0095 46 PRINT 21,(I,W(NWX+I),I=1,N)
0096 PRINT 23,FMIN
0097 IF (I PRINT) 39,39,143
0098 143 PRINT 22,(I,W(NWF+I),I=1,M)
0099 39 GO TO (49,47,47,48),IS
C STORE THE INITIAL VECTORS X AND F
0100 48 IF (I) 50,50,51
0101 50 DO 52 I=1,N
0102 W(NWX+I)=X(I)
0103 52 CONTINUE
0104 GO TO 54
C CALCULATE THE INITIAL JACOBIAN APPROXIMATION
0105 51 K=IC
0106 DO 55 I=1,M
0107 W(K)=(F(I)-W(NWF+I))/CSTEP
0108 K=K+N
0109 55 CONTINUE
C TEST WHETHER THE MOST RECENT X IS BEST
0110 56 X(IC)=W(NWX+IC)
0111 IF (FMIN-FSQ) 56,56,57
0112 GO TO 58
0113 57 W(NWX+IC)=X(IC)
0114 DO 53 I=1,M
0115 W(NWF+I)=F(I)
0116 53 CONTINUE
0117 FMIN=FSQ
C SET X FOR THE NEXT CALL OF CALFUN
0118 IC=IC+1
0119 IF (IC-N) 59,59,60
0120 59 X(IC)=W(NWX+IC)+DSTEP
0121 GO TO 3
C SET THE DIRECTION MATRIX
0122 60 K=NWD
0123 DO 61 I=1,N
0124 DO 62 J=1,N
0125 K=K+1
0126 W(K)=C.OOO
0127 CONTINUE
0128 W(K+I-N)=1.D0
0129 W(NWC+I)=1.D0+DFLOAT(N-1)
0130 61 CONTINUE
C SET THE MARQUARDT PARAMETER TO ITS LEAST VALUE
0131 24 PAR=PARM
C COPY THE JACCEIAN AND APPEND THE MARQUARDT MATRIX
0132 25 PPAR=PAR*PAR
0133 NIPAR=0

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0134      KK=0
0135      K=NWI+1
0136      DO 26 I=1,N
0137      DC 141 J=1,M
0138      KK=KK+1
0139      W(KK+NWI)=W(KK)
0140      CONTINUE
0141      DO 27 J=1,N
0142      K=K+1
0143      W(K)=0.000
0144      CONTINUE
0145      W(K+1-N)=PAR
0146      CONTINUE
0147      C
0148      C CALCULATE THE GENERALIZED INVERSE OF J
0149      C CALL MRLAD(N,M,N,W(NWI+1),N,W(NWI+1))
0150      C NOTE THAT THE THIRD AND FIFTH ENTRIES OF THIS ARGUMENT LIST
0151      C START FOR ONE-DIMENSIONAL ARRAYS.
0152      C START THE ITERATION BY TESTING FMIN
0153      C IF (FMIN-ACC) 7,7.65
0154      C NEXT PREDICT THE DESCENT AND MARQUARDT MINIMA
0155      DS=0.000
0156      DN=0.000
0157      SP=0.000
0158      DO 66 I=1,N
0159      X(I)=0.000
0160      F(I)=0.000
0161      K=1
0162      DO 67 J=1,M
0163      X(I)=X(I)-W(K)*W(NWI+K)*W(NWI+J)
0164      F(I)=F(I)-W(NWI+K)*W(NWI+J)
0165      K=K+1
0166      CONTINUE
0167      DS=DS+X(I)*X(I)
0168      DN=DN+F(I)*F(I)
0169      SP=SP+X(I)*F(I)
0170      CONTINUE
0171      PREDICT THE REDUCTION IN F(X) DUE TO THE MARQUARDT STEP
0172      AND ALSO PREDICT THE LENGTH OF THE STEEPEST DESCENT STEP
0173      PRED=SP+SP
0174      DMULT=0.000
0175      K=0
0176      DO 68 I=1,M
0177      AD=0.000
0178      DO 69 J=1,N
0179      K=K+1
0180      AF=AD+W(K)*F(J)
0181      AD=AD+W(K)*X(J)
0182      CONTINUE
0183      PRED=PRED-AP*AP
0184      DMULT=DMULT+AD*AD
0185      CONTINUE
0186      TEST FOR CONVERGENCE
0187      IF (DN-DM) 28,28.29
0188      AP=DS CRT(DN)
0189      IF (PRED+2.000*PPAF*AP*(CMAX-AP)-ACC) 770,770.70
0190      IF (PRED+PPAF*(DM-DN)-ACC) 770,770.70
0191      WRITE(6,771)
0192      FORMAT(1H,'PREDICTED REDUCTION IN F(X) IS LESS THAN ACC')
0193      771

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0185      GO TO 7
0186      C      TEST WHETHER TO APPLY THE FULL MARQUARDT CORRECTION
0187      70 DMULT=DS/DMULT
0188      CS=DS*DMULT*DMULT
0189      71 IS=2
0190      IF (DN-DD) 72,72,73
0191      C      TEST THAT THE MARQUARDT PARAMETER HAS ITS LEAST VALUE
0192      72 IF (PAR-PARM) 30,30,24
0193      30 DD=DMAX1(DN,DSS)
0194      DS=0.2500*DN
0195      YINC=1.000
0196      IF (DN-DSS) 74,132,132
0197      74 IS=3
0198      GO TO 103
0199      C      TEST WHETHER TO INCREASE THE MARQUARDT PARAMETER
0200      73 IF (DN-DPAR) 31,31,32
0201      31 NTPAR=0
0202      GC TO 33
0203      32 IF (NTPAR) 34,34,35
0204      34 NTPAR=1
0205      PTM=DN
0206      GO TO 33
0207      35 NTPAR=NTPAR+1
0208      PTM=DMINI(PTM,DN)
0209      IF (NTPAR-NT) 33,36,36
0210      C      SET THE LARGEN VALUE OF THE MARQUARDT PARAMETER
0211      36 PAR=PAR*(PTM/DM)**0.2500
0212      137 AP=DSQRT(PRED/DN)
0213      IF (AP-PAR) 25,25,138
0214      138 PAR=DMINI(AP,PAR*(DM/(6.000*CC))**0.2500)
0215      GO TO 25
0216      C      TEST WHETHER TO USE THE STEEPEST DESCENT DIRECTION
0217      33 IF (DS-DD) 75,76,76
0218      C      TEST WHETHER THE INITIAL VALUE OF DD HAS BEEN SET
0219      76 IF (CC) 77,77,78
0220      77 DD=DMINI(DM,DS)
0221      IF (CC-DSS) 79,78,78
0222      79 DD=DSE
0223      GO TO 71
0224      C      SET THE MULTIPLIER OF THE STEEPEST DESCENT DIRECTION
0225      78 ANMUL=0.00
0226      DMULT=DMULT*DSQRT(DD/DS)
0227      GC TO 80
0228      C      INTERPOLATE BETWEEN THE STEEPEST DESCENT AND MARQUARDT DIRECTIONS
0229      75 SP=SP*DMULT
0230      ANMUL=(DD-DJ)/((SP-DS)+DSQRT((SP-DC)**2+(DN-CC)*(DD-DJ)))
0231      DMULT=DMULT*(1.0000-ANMUL)
0232      C      CALCULATE THE CORRECTION TO X, AND ITS ANGLE WITH THE FIRST
0233      DIRECTION
0234      80 DN=0.000
0235      SP=0.000
0236      DO 81 I=1,N
0237      F(I)=DMULT*X(I)+ANMUL*F(I)
0238      DN=DN+F(I)*F(I)
0239      SP=SP+F(I)*F(NWD+I)
0240      81 CCNT=CCNT+1
0241      DS=0.2500*DN
0242      C      TEST WHETHER AN EXTRA STEP IS NEEDED FOR INDEPENDENCE
0243      82
0244      83
0245      84
0246      85
0247      86
0248      87
0249      88
0250      89
0251      90
0252      91
0253      92
0254      93
0255      94
0256      95
0257      96
0258      97
0259      98
0260      99
0261      100
0262      101
0263      102
0264      103
0265      104
0266      105
0267      106
0268      107
0269      108
0270      109
0271      110
0272      111
0273      112
0274      113
0275      114
0276      115
0277      116
0278      117
0279      118
0280      119
0281      120
0282      121
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0233      IF (W(NWC+1)-DTESI) 122,132,82
0234      IF (SP*SP-DS) 83,132,132
C          TAKE THE EXTRA STEP AND UPDATE THE DIRECTION MATRIX
0235      DO 94 I=1,N
0236      X(I)=W(NWC+1)+DSTEP*W(NWC+1)
0237      W(NWC+1)=W(NWC+1)+1.00
0238      CONTINUE
0239      W(NWD)=1.00
0240      IF(N.LE.1)GO TO 4
0241      DO 95 I=1,N
0242      K=NWD+I
0243      SP=W(K)
0244      DO 86 J=2,N
0245      W(K)=W(K+N)
0246      K=K+N
0247      CONTINUE
0248      W(K)=SP
0249      CONTINUE
0250      GO TO 4
C          EXPRESS THE NEW DIRECTION IN TERMS OF THOSE OF THE DIRECTION
C          MATRIX, AND UPDATE THE COUNTS IN W(NWC+1) ETC.
0251      132 IF(N.CE.2)GO TO 153
0252      IS=1
0253      GO TO 152
0254      153 SP=0.00
0255      K=NWD
0256      DO 87 I=1,N
0257      X(I)=DW
0258      DW=0.000
0259      DO 83 J=1,N
0260      K=K+I
0261      DW=D*F(J)*(K)
0262      CONTINUE
0263      GO TO (89,90),IS
0264      W(NWC+1)=W(NWC+1)+1.00
0265      SP=SP+DW*DW
0266      IF (SP-DS) 87,87,91
0267      91 IS=1
0268      KK=I
0269      X(I)=DW
0270      GO TO 92
0271      X(I)=DW
0272      W(NWC+1)=W(NWC+1)+1.00
0273      97 CONTINUE
0274      W(NWD)=1.00
C          REORDER THE DIRECTIONS SO THAT KK IS FIRST
0275      IF (KK-1) 93,93,94
0276      94 KS=NWC+KK*N
0277      K=KS+1
0278      SP=W(K)
0279      DO 96 J=2,KK
0280      W(K)=W(K-N)
0281      K=K-N
0282      CONTINUE
0283      W(K)=SP
0284      CONTINUE
0285      GENERATE THE NEW CRYSTALLOGRAPHIC DIRECTION MATRIX
C          93 DO 97 I=1,N
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0307 W(NW+1)=0.00
0308 17 CONTINUE
0309 SP=X(1)*X(1)
0310 K=NW
0311 DC 08 I=2,N
0312 CS=SQRT(SP*(SP+X(I)*X(I)))
0313 CW=SP/DS
0314 DS=X(1)/DS
0315 SP=SP+X(I)*X(I)
0316 DC 09 J=1,N
0317 K=K+1
0318 W(NW+J)=W(NW+J)+X(I-1)*W(K)
0319 W(K)=DW*W(K+N)-DS*W(NW+J)
0320 93 CONTINUE
0321 08 CONTINUE
0322 SP=1.000/DSQRT(DN)
0323 DC 10 C I=1,N
0324 K=K+1
0325 W(K)=SP*F(I)
0326 100 CONTINUE
0327 152 FV=0.000
0328 C 100 PREDICT THE NEW RIGHT HAND SIDES
0329 K=0
0330 DC 101 I=1,M
0331 W(NW+I)=W(NW+I)
0332 DC 102 J=1,N
0333 K=K+1
0334 W(NW+I)=W(NW+I)+W(K)*F(J)
0335 FNF=NP+W(NW+I)**2
0336 102 CONTINUE
0337 101 CONTINUE
0338 C 103 CALCULATE THE NEXT VECTOR X, AND THEN CALL CALFUN
0339 DC 104 I=1,N
0340 X(I)=W(NW+I)+F(I)
0341 104 CONTINUE
0342 GO TO 4
0343 C 4 UPDATE THE STEP SIZE
0344 DMULT=0.900*FMIN+0.100*FNF-FSC
0345 IF (DMULT) 105,106,108
0346 105 DD=DMAX1(DSS,0.250*DD)
0347 TINC=1.000
0348 IF (FSC-FMIN) 106,107,107
0349 TRY THE TEST TO DECIDE WHETHER TO INCREASE THE STEP LENGTH
0350 SP=0.000
0351 SS=0.000
0352 DC 105 I=1,M
0353 SP=SP+DABS(F(I)*(F(I)-W(NW+I)))
0354 SC=SS+(F(I)-W(NW+I))**2
0355 106 CONTINUE
0356 PJ=1.000+DMULT/(SP+DSQRT(SP*SP+DMULT*SS))
0357 SP=DMIN1(A.000,TINC,PJ)
0358 TINC=PJ/SP
0359 DD=DMIN1(DM,SP*DD)
0360 GO TO 106
0361 C 47 IF F(X) IMPROVES STORE THE NEW VALUE OF X
0362 106 FMIN=FSC
0363 DC 111 I=1,N
0364 SP=X(I)

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0341      X(I)=W(NWX+I)
0342      W(NWX+I)=SP
0343      CONTINUE
0344      DO 112 I=1,M
0345      SP=F(I)
0346      F(I)=W(NWF+I)
0347      W(NWF+I)=SP
0348      CONTINUE
0349      DO 110 J=1,N
0350      IS=2
0351      IF (FMIN-ACC) 7,7,93
0352      C      CALCULATE THE CHANGES IN X AND IN F
0353      DO 107 DS=0.0D0
0354      DO 114 I=1,N
0355      X(I)=X(I)-W(NWX+I)
0356      DS=DS+X(I)*X(I)
0357      CONTINUE
0358      DO 115 I=1,M
0359      F(I)=F(I)-W(NWF+I)
0360      C      CALCULATE THE GENERALIZED INVERSE TIMES THE CHANGE IN X
0361      K=NI
0362      SS=0.0D0
0363      DO 116 I=1,M
0364      SP=0.0D0
0365      DO 117 J=1,N
0366      K=K+1
0367      SP=SP+W(K)*X(J)
0368      CONTINUE
0369      W(NWV+I)=SP
0370      SS=SS+SP*SP
0371      CONTINUE
0372      C      CALCULATE J TIMES THE CHANGE IN F
0373      C      ALSO APPLY PROJECTION TO THE GENERALIZED INVERSE
0374      DO 118 I=1,N
0375      ST=0.0D0
0376      K=NI+1
0377      DO 119 J=1,M
0378      ST=ST/SS
0379      K=NI+I
0380      DO 120 J=1,M
0381      W(K)=W(K)-ST*W(J+NWV)
0382      K=K+N
0383      CONTINUE
0384      ST=SPAR*X(I)
0385      K=I
0386      DO 121 J=1,M
0387      ST=ST+W(K)*F(J)
0388      K=K+N
0389      CONTINUE
0390      W(NWV+I)=ST
0391      CONTINUE
0392      C      REVISE J AND CALCULATE ROW VECTOR FOR CORRECTION TO INVERSE
0393      IC=0
0394      K=0
0395      KK=NWV

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0105      SP=0.000
0106      SPP=0.000
0107      DO 122 I=1,M
0108      SS=F(I)
0109      ST=F(I)
0110      DO 123 J=1,N
0111      IC=IC+1
0112      KK=KK+1
0113      SS=SS-W(IC)*X(J)
0114      ST=ST-W(KK)*W(NMW+J)
0115      123 CONTINUE
0116      SS=SS/DO
0117      W(NMW+1)=ST
0118      SP=SP+F(I)*ST
0119      SPP=SPP+ST*ST
0120      DO 124 J=1,N
0121      KK=KK+1
0122      W(K)=W(K)+SS*X(J)
0123      124 CONTINUE
0124      122 CONTINUE
0125      DO 125 I=1,N
0126      ST=DAP*X(I)
0127      DO 126 J=1,N
0128      KK=KK+1
0129      ST=ST-W(KK)*W(NMW+J)
0130      126 CONTINUE
0131      W(NWT+1)=ST
0132      SP=SP+PAR*X(I)*ST
0133      SPP=SPP+ST*ST
0134      125 CONTINUE
0135      C      TEST THAT THE SCALAR PRODUCT IS SUFFICIENTLY ACCURATE
0136      C      IF(0.0100*SPP-DABS(SPP-SPP))63.63.127
0137      C      CALCULATE THE NEW GENERALIZED INVERSE
0138      DO 127 I=1,N
0139      KENWI+1
0140      ST=X(I)
0141      DO 128 J=1,M
0142      ST=ST-W(K)*F(J)
0143      KK+1
0144      128 CONTINUE
0145      SS=0.000
0146      DO 129 J=1,N
0147      SS=SS+W(K)*X(J)
0148      KK+1
0149      129 CONTINUE
0150      ST=(ST-PAR*SS)/SP
0151      KENWI+1
0152      DO 131 J=1,M,N
0153      W(K)=W(K)+ST*W(NMW+J)
0154      KK+1
0155      131 CONTINUE
0156      128 CONTINUE
0157      GO TO 64
0158      END

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APPENDIX E

ON THE POSSIBILITY OF EXPERIMENTAL SEPARATION OF
RESONANCES AND CUSPS FROM BACKGROUND IN ELECTRON SCATTERING

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Abstract

It is demonstrated with the help of model calculations that a laser field can be used to suppress the background in electron scattering cross sections and to pick out only those parts which are rapidly varying as function of the incoming electron energy. Therefore it becomes possible to measure the pure Breit-Wigner peaks and threshold effects independent of the fact that interference between the resonances and the background in radiationless electron scattering is strong. The results are interpreted within the low frequency limit for free-free transitions. The AC Stark shift of the resonance is also observed.

1. Introduction

Some of the most spectacular physics in electron-atom scattering is in the appearance of resonances and threshold effects. Unfortunately, in many cases these effects are small structures buried in a big background and their shape is usually modified by interference with the background. Sometimes it is difficult to be sure if a measured structure is real or noise and sometimes it is hard to pull the interesting physical parameters out of the measured data. For a review of these effects and their experimental difficulties see ref.1. If on the other hand, an experimentalist were able, by some method, to suppress all the background in the neighborhood of a resonance, then a pure Breit-Wigner peak would be observed and it would be straightforward to determine the position E_R and the width Γ of this resonance. The purpose of this paper is to explain a method of performing an electron scattering experiment in such a way that only those parts of the scattering amplitude lead to a signal, which vary rapidly as function of the incoming electron energy. Thereby we pick resonances and cusps out of the total scattering amplitude and get rid of all background influences.

The basic idea is to perform the electron scattering process within a strong laser field and to collect only those scattered electrons which have emitted or absorbed a certain number of photons. This method has been suggested first in ref.2 in a treatment of free-free transitions in first order perturbation theory and low frequency limit.

It will become clear in this paper that the idea works under much more general circumstances. Processes in which an electron scatters off an atom or molecule and emits or absorbs photons at the same time are known under the name free-free transitions. (For a review of these processes see ref.3). In these processes three systems (electron, target, laser field) interact with each other and this makes a theoretical treatment so complicated that up to now only special cases and approximations have been investigated. If the photon energy is far away from all transition energies of the target states involved in the process then the interaction between the laser and the target can to a high degree of approximation be neglected and the problem reduces to the description of electrons under the simultaneous influence of the target potential and the laser field. To check this the

influence of the laser-target interaction on the processes considered here can be estimated by the following considerations: The external field induces an electric dipole moment in the target atom and this dipole field can be felt by the scattered electron and can thereby modify the electron-target interaction potential V . Next let us estimate the order of magnitude of this effect. In most of our calculations a photon energy of 0.005 a.u. is used which is close to the CO_2 laser photon energy of 117 meV. Because this photon energy is smaller by a factor 10 to 100 compared to the first excitation energy of the

atomic ground states we use the static polarizability to calculate the induced dipole moment (Thereby we overestimate the effect). For atoms the polarizability is between $2 \cdot 10^{-25} \text{ cm}^3$ (in e.s. units) for such a small closed shell atom like Helium and $400 \cdot 10^{-25} \text{ cm}^3$ for such a big alkali atom like Cesium.

↳ To see strong signals in free-free transitions we need laser power fluxes in the order of 10^8 Watt/cm^2 and for a CO_2 laser this corresponds to an electric field amplitude of 270000 V/cm or 900 e.s.u.. Therefore the induced dipole moment is between $1.8 \cdot 10^{-22} \text{ e.s.u.}$ and $3.6 \cdot 10^{-20} \text{ e.s.u.}$ for the various atoms. A scattering electron at a distance of 10^{-8} cm , which is in the order of magnitude of the average distance of an electron in a resonance state from the atomic center, will feel a potential energy E_d of a magnitude between 10^{-3} eV and 10^{-1} eV . In electron scattering dipole effects are usually of importance only at very low energy where the electron-dipole interaction energy E_d is of the same order of magnitude as the kinetic energy E_i of the electron. In the case considered here $E_d/E_i \approx 0.01$ in the worst case. Therefore it seems to be justified to neglect the laser-atom interaction.

This neglect of the laser-target interaction does not of course apply at all to molecules which have vibrational transition energies close to the photon energy. In general, the laser frequency must be far out of resonance with the target system.

In addition the laser field strength considered here is small compared to the internal field in the atoms and therefore it is not necessary to worry about the ionization of the target.

Now even this simplified problem without laser-target interaction has not yet been solved in general. Various treatments have either treated the laser field in perturbation expansion or have used the low frequency approximation. The method used here to suppress the background can be interpreted theoretically in the low frequency limit. The relevant ideas of this approximation will be given later in section 3 (For some additional information about more general aspects of the low frequency approximation see refs. 4-7).

To fully appreciate the method it is perhaps better to forget about formal theories and instead to make some simple model calculations in the spirit of a numerical experiment. In section 2 we investigate in this way what may happen in an experiment since up to now the new method has not yet been realized in the laboratory. As such we construct a simple 1-dimensional model, which can be solved in terms of known functions. We do not use the low frequency approximation and we do not make a perturbation expansion of the electron-laser interaction. The approximations we must make are the neglect of the laser-target interaction, mentioned above, the dipole approximation and a cut off of the photon Fock space due to the inability to numerically

handle more than a finite number of photon number states. In practice this is not a problem as all reported results, upon inclusion of further photon states in the model, do not significantly change.

In section 3 we present a theoretical interpretation of our numerical results. Section 4 contains conclusions and final remarks and some suggestions onto how to optimise possible experiments. In the appendix we explain our model in detail and show how we calculate all transition amplitudes in terms of known functions.

We use atomic units for all numbers throughout the whole rest of the paper.

2. Results of the numerical experiments

We take a scattering problem in 1 dimension and represent the target by a 2-state system with an excitation energy $E_{12}=0.6$. We assume that this target provides a 2-channel square well potential V to the incoming electron (see fig.1). In each figure below we have indicated the special choice of V used. We always start the process with the target in its lower state. If the laser is switched off and the incoming kinetic energy E_i of the electron is below 0.6 then the electron may either be transmitted or reflected without energy change. We denote this probability for transmission by T_{rl} and the probability for reflexion by R_{rl} (rl is an abbreviation for "radiationless"). If E_i is above 0.6 the electron may excite the target and leave it in its upper state. We denote the probability for excitation in radiationless transmission by S_{rl} and the probability for excitation in radiationless reflexion by Q_{rl} . S_{rl} and Q_{rl} exist only for $E_i > 0.6$.

If we switch on the laser field, then the electron can, in addition to the above, exchange energy with the field in integer multiples of the photon energy ω . We denote the probabilities for processes in which the electron gains (loses) the energy $N\omega$ from the field by Q_N, R_N, S_N, T_N respectively. $R_N(E_i)$ is the probability that an electron comes in with initial kinetic energy E_i , hits the target, is reflected leaving the target behind in its lower state and flies away with a final kinetic energy $E_f = E_i + N\omega$.

Similarly, $Q_N(E_i)$ is the probability that the electron comes in with energy E_i , hits the target, is reflected leaving the target behind in its upper state and flies away with final energy $E_f = E_i - E_{12} + N\omega$. $T_N(E_i)$ and $S_N(E_i)$ are the probabilities for the corresponding processes in transmission. Of course, $Q_N(E_i)$ and $S_N(E_i)$ only exist for $E_f > 0$ i.e. $E_i + N\omega > E_{12}$. The quantities Q, R, S, T are the 1-dimensional analogs to the differential cross sections in 3 dimensions.

In fig.2 we have chosen a potential V which causes an elastic scattering resonance at an incoming energy of $E_R \approx 0.233$ with a width of $\Gamma \approx 0.0002$. This Γ is in the same order as the natural width of electron-rare gas atom resonances. The energy E_R is far below the threshold at $E_T = 0.6$ and therefore no excitation of the target is possible near this energy. In the top line of fig.2 we show the quantities $T_{r1}(E_i)$ on the left and $R_{r1}(E_i)$ on the right as functions of E_i . Below we show the quantities $T_N(E_i)$ and $R_N(E_i)$ as functions of E_i for several values of N . The photon energy is always $\omega = 0.005$ which is close to the photon energy of a CO_2 laser. The power density of the field is so big that the quantity $\alpha = eA / mc \hbar \omega$ has a magnitude of exactly 1. (e is the electron charge, m is the electron mass, c is the speed of light, A is the amplitude of the vector potential). This is still a moderate power density and therefore only one photon processes give a strong signal. Two photon transitions can just be seen. In fig.3 we show the results for a calculation in which we have increased the laser

power so that $\alpha = 2$ but left all other parameters unchanged.

The important results of these figures are: The elastic resonance causes a whole series of resonances in each R_N and T_N but only a few ones are strong enough so that we can observe them immediately. The distance between two adjacent structures is exactly ω . The strength of the individual structures depends on the laser power. In general we see more resonances if we increase the laser power. The most striking observation is, that in $T_N, N \neq 0$ there is no background at all and the resonances appear as pure Breit-Wigner peaks. In all other cases (i.e. for T_0 and all R_N) the interference of the resonances with the background is either similar to the corresponding radiationless case only with the difference that the relative resonance effect is smaller or the resonance shape is reflected compared to the radiationless case. The best examples for this reflection are in R_{+1} in fig.3. We see that it is easier to determine E_R and Γ out of T_{+1} or T_{-1} than out of T_{r1} or R_{r1} . In fig.2 note that T_N and T_{-N} or R_N and R_{-N} look similar in shape but are shifted by $N\omega$.

In fig.4 we have changed the offdiagonal elements of V so that the width Γ of the elastic resonance is now 0.0012 which is in the order of the resolution of common electron spectrometers. This change in V causes also a small shift in the position E_R of the resonance (see the top line in fig.4). All other parameters are the same as in fig.2. The width Γ is now so big that there are overlaps of the

various resonance structures in R_N and T_N which influence the resonance shapes in general. For $T_N, N \neq 0$ the wings of two adjacent resonance peaks simply add without any visible interference. Again T_N and T_{-N} or R_N and R_{-N} look similar in shape but shifted by $N\omega$. In fig.5 we show the resonance curves for $\alpha=3$ and otherwise the same parameters as in fig.4. We did not make calculations with another value of ω because the interesting quantity is the ratio between ω and Γ and a increase of ω would cause similar effects as a decrease of Γ .

The only threshold of our 2-channel model is at $E_T=0.6$ and it is interesting to compare radiationless scattering and free-free transitions close to this energy. Fig.6 shows radiationless scattering in the top line and free-free transitions below. In the drawings T and R are represented by solid lines and S and Q are represented by dotted lines. First we see that in free-free transitions the threshold for S_N and Q_N lies at $E_i = E_T - N\omega$. This is easy to understand because the energy which the electron gains/losses from the laser field goes into the energy balance for the excitation of the target by the electron impact and the new channel opens as soon as the final kinetic energy of the electron is above zero i.e. as soon as $E_i + N\omega - E_T > 0$, or $E_i > E_T - N\omega$. In T_{-1} we see a plateau between E_T and $E_T + \omega$ and in T_{+1} a plateau between $E_T - \omega$ and E_T with a sharp drop on both sides. In addition there are smaller threshold effects shifted by ω away from the sharp drops. In T_{-2} and T_{+2} we see a sharp peak at $E_T + \omega$ or $E_T - \omega$

respectively and again smaller effects shifted away by ω . In the other cases (T_0 and all R_N) the threshold effects occur at various $E_i = E_T + n\omega$ and their shape is either of the same type as in the corresponding radiationless scattering or it is just turned upside down. In S_N and Q_N there are only very weak structures, too weak to be seen clearly in fig.6.

In fig.7 we see results for $\alpha = 2$ and otherwise the same parameters as in fig.6. Now the threshold effects are distributed over more energy values and for example in T_{-1} the main drop on both sides of the plateau is shifted outwards by ω on both sides compared to fig.6. In the picture for Q_0 we see an "accidental" zero near $E_i = 0.607$ which will be explained below. In fig.8 we see results for $\omega = 0.002$ and otherwise the same parameters as in fig.6. All curves look nearly the same as in fig.6 only the energy scale is changed by a factor 2.5 which is the ratio between the photon energies in the two examples.

The most important results for the thresholds are in summary: A sudden drop (or increase) in the radiationless scattering as function of the incoming energy produces in the free-free probabilities T_{+1} and T_{-1} a plateau near the threshold energy and zero signal otherwise. At moderate laser power the length of the main structure is exactly ω . Thereby the presense or absense of a threshold makes a 100% change in the relative signal strength but the absolute signal strength is always very low. Depending on

the values of ω and α the strong contributions to the threshold effects in T_N appear at different energies.

3. Interpretation of the numerical results

A theoretical explanation of the results of section 2 can be given most easily within the low frequency approximation and therefore let us first explain its basic idea. In order to be more general we give all formulas for the 3-dimensional case and consider the numerical results from section 2 as the special cases of the scattering angles 0 and π . If the laser wavelength is very long compared to atomic distances, then we can separate the free-free transition into three steps. First a free electron moves within the laser field and can virtually emit and absorb photons. Let us assume that the laser field is single mode and in the pure number state $|N\rangle$ in absence of the electron. We denote the state of a free electron moving with momentum \vec{p} by $|\vec{p}\rangle$. If we neglect photon depletion effects and use the dipole approximation, then the exact state of the electron in the field is given by (see appendix)

$$|\phi_{\vec{p}, N}\rangle = \sum_n J_n(\vec{\alpha} \cdot \vec{p}) |\vec{p}\rangle |N+n\rangle \quad (1)$$

J_n is the Bessel function of first kind and order n .

$\vec{\alpha} = eA \vec{\epsilon} / mc \hbar \omega$ where $\vec{\epsilon}$ is the polarization vector of the laser field. This $\vec{\alpha}$ is the 3-dimensional generalization of the α given above in section 2.

The Bessel functions $J_n(\vec{\alpha} \cdot \vec{p})$ can be viewed as interaction coefficients for virtual n photon absorption/emission at absence of a target.

In dipole approximation there is no recoil of the electron during emission or absorption of a photon and therefore the electron momentum does not depend on how many photons the electron has absorbed or emitted i.e. $|\vec{p}\rangle$ in (1) is independent of n . The energy of the electron is different in its various states and the electron wave connected with the photon number state $|N+n\rangle$ is at energy $E = p^2/2m - n\omega$. Only the $n=0$ term is on the energy shell and all other terms are off shell.

Then in the second step of the free-free transition this mixture of electron waves hits the target and is scattered. The main idea of the low frequency approximation is to neglect the laser-electron interaction during this second step and therefore the electron-target scattering is described by a radiationless scattering amplitude. But according to what was said above each term of the sum in (1) is scattered at its particular intermediate energy $E_i - n\omega$ and its scattering is therefore described by a scattering amplitude at this shifted energy.

In the third step the scattered electron waves interact again with the laser and evolve into their final states.

Along these lines the following formula (3) has been derived first in ref.8 and confirmed later in ref.9 by another derivation. This formula gives the scattering

amplitude $f_N(E_i, \vartheta)$ for an electron to come in with kinetic energy E_i , be scattered by an angle ϑ and to have a final kinetic energy E_f of

$$E_f = E_i + N \omega \quad (2)$$

$$f_N(E_i, \vartheta) = \sum_k J_{N-k}(\vec{\alpha} \vec{p}_f) f_{r1}(E_i + k\omega, \vartheta) J_k(-\vec{\alpha} \vec{p}_i) \quad (3)$$

f_{r1} is the corresponding amplitude for radiationless electron-target scattering. The three factors correspond to the three physical stages above. An analogous formula holds for scattering with excitation of the target if we take on the r.h.s. of (3) the corresponding scattering amplitude for radiationless excitation of the target and take the excitation energy into the energy balance (2).

Now let us decompose f_{r1} in (3) into a resonance part and a background part

$$f_{r1}(E_i + k\omega, \vartheta) = f_{r1}^R(E_i + k\omega, \vartheta) + f_{r1}^{BG}(E_i + k\omega, \vartheta) \quad (4)$$

The Bessel functions decrease rapidly for increasing order and fixed argument as soon as the absolute value of the order becomes larger than the absolute value of the argument. Therefore only a few k give a strong contribution

to the k sum in (3). ^{Since} f_{r1}^{BG} depends only weakly on its energy argument then we can neglect this dependence, take all f_{r1}^{BG} at the energy E_i , pull f_{r1}^{BG} out of the k sum and apply the addition theorem of the Bessel functions and find

$$f_N(E_i, \vartheta) = J_N(\vec{\alpha}(\vec{p}_f - \vec{p}_i)) f_{r1}^{BG}(E_i, \vartheta) + \sum_k J_{N-k}(\vec{\alpha} \vec{p}_f) f_{r1}^R(E_i + k\omega, \vartheta) J_k(-\vec{\alpha} \vec{p}_i) \quad (5)$$

Our model calculation is independent of the low frequency

approximation and so a comparison between the exact numerical results of sec.2 and (5) can be viewed as test of (5).

The present state of the experimental verification of (5) is as follows: In ref.10 $|f_N|^2$ has been measured as function of N for several values of ϑ, E_i, \vec{e} . All results are in qualitative agreement with (5). It has not been possible to check for quantitative agreement because the exact laser power distribution in space and time has not been known. For quantitative calculations its knowledge would be absolutely necessary since multiphoton transitions are a nonlinear effect and depend essentially on the exact power distribution in space and time and not only on the average power (For these problems see also ref.11). In ref.10 resonances did not play any role and therefore only the first term in (5) has been measured. From such a measurement we cannot, in contrast to the present work, learn anything new about electron-atom scattering because the result is essentially the product of the elastic background cross section and a Bessel function - both well known quantities.

In refs.12,13 $|f_{-1}|^2$ has been measured as function of E_1 near the argon resonances at 11eV but unfortunately only in backward direction for the one scattering angle $\vartheta = 160^\circ$. Since a weak laser has been used only the resonance structures at E_R and $E_R + \omega$ could be seen. Their shape and strength is in full agreement with (5).

For scattering without excitation of the target $|p_i| \approx |p_f|$ since $\omega \ll E_i$ and therefore in forward direction we find

$\vec{\alpha}(\vec{p}_f - \vec{p}_i) \approx 0$. The background term in (5) disappears in forward direction for $N \neq 0$ because $J_N(0) = \delta_{N,0}$. This is the explanation why we did not see a background contribution for $T_N, N \neq 0$ in the model calculations. f_{r1}^R produces a resonance structure when its energy argument is at E_R and therefore we get a resonance structure in the k -sum in (5) every time when $E_i + k\omega = E_R$ for a $k \in \mathbb{Z}$. The magnitude of the resonance effect at $E_i = E_R - k\omega$ depends on the exact value of the two Bessel functions in the corresponding term in (5). If $\Gamma \ll \omega$ we get a series of well separated resonances with an energy spacing ω between adjacent peaks. This is exactly what we saw in figs. 2-5.

In backward direction $\vec{p}_f \approx -\vec{p}_i$ and in general $J_N(\vec{\alpha}(\vec{p}_f - \vec{p}_i))$ is not near a zero and the background does not disappear. Depending on the relative signs of the various Bessel functions the relative phase between the resonance term and the background term is either the same as in the radiationless case or it is just shifted by π . Therefore the resonance shape is either the same as in the radiationless case or it is just reflected. The magnitude of the relative resonance effects depends again on the exact values of the corresponding Bessel functions and thereby on the parameters E_i, α . We saw that T_N and T_{-N} or R_N and R_{-N} look nearly the same in shape but are only shifted by $N\omega$. This can be explained by the fact that $J_N = (-1)^N J_{-N}$.

One effect which is not contained in (5) is the AC Stark shift of the resonances. Let us look at fig. 9.

In this figure we show resonance structures in T_N and R_N at various initial energies $E_i = E_R + k\omega$ and for various values of ω , α and N . The potential V is the same as in figs. 2 and 3. In each picture we show the low frequency approximation of (3) as broken line and the exact numerical result as solid line. We see a shift of the resonance structures which does not depend on E_i , N and \mathcal{V} but depends on ω and α . Besides this shift the low frequency limit gives the correct shape and height for all resonance peaks. The fact that the shift does not depend on the particular peak at which we look i.e. does not depend on E_i , N and \mathcal{V} is an indication that the resonance itself is shifted and not only its appearance in the free-free transitions. The Stark shift goes quadratically with ω and quadratically with α . This is in exact agreement with the results of ref. 9. In our examples in fig. 9 the shift $\Delta E_R \approx -0.25 \omega^2 \alpha^2$. According to ref. 9 the proportionality constant between ΔE_R and $\omega^2 \alpha^2$ is a measure of the laser induced coupling between the resonance wave function φ_2 in channel 2 and the continuum wave function φ_1 in channel 1. Therefore a measurement of $\Delta E_R / \omega^2 \alpha^2$ could give experimental information about the dipole matrix element $\langle \varphi_1 | \vec{E} \vec{p} | \varphi_2 \rangle$.

We could not see a change of Γ with increasing laser power. For this extra width caused by the Stark decay to become important much higher laser powers would be necessary.

Now let us try to explain the threshold effects in figs.6-8 by making a quite crude model for a threshold effect in radiationless scattering and representing the amplitude for scattering without target excitation by

$$f_{r1}(E_i, \vartheta) = c(\vartheta) + \Theta(E_i - E_T) d(\vartheta) \quad (6)$$

where c and d do not depend on E_i and Θ is the unit step function. If we insert (6) into (5) we get

$$f_N(E_i, \vartheta) = c(\vartheta) J_N(\vec{\alpha}(\vec{p}_f - \vec{p}_i)) + d(\vartheta) \sum_k J_{N-k}(\vec{\alpha} \vec{p}_f) \Theta(E_i + k\omega - E_T) J_k(-\vec{\alpha} \vec{p}_i) \quad (7)$$

For $\vec{p}_f \approx \vec{p}_i$ and $N \neq 0$ the first term drops. The second term produces a step at each $E_i = E_T - k\omega, k \in \mathbb{Z}$. The relative strength of the various steps depends on the exact values of the Bessel functions and thereby on the values of the parameters E_i and α .

If we set $\vartheta = 0$ in (7) and assume a moderate laser power for which only first order contributions are important, we obtain

$$f_{-1}(E_i, 0) = \frac{1}{2} \alpha |p| d(0) \left\{ \Theta(E_i - E_T) - \Theta(E_i - \omega - E_T) \right\}$$

This is just a plateau between E_T and $E_T + \omega$ and it is zero otherwise. An analogous calculation applies to T_{+1} and gives a plateau between $E_T - \omega$ and E_T . T_{r1} in fig.6 does not have a sharp step at E_T but a rounded one and therefore also T_{+1} and T_{-1} have a rounded drop off on both sides of the plateau.

We see additional smaller threshold effects at other E_i which come from higher order contributions. For higher laser powers as e.g. in fig.7 higher order contributions

may become more important than first order contributions and therefore the steps at other E_i become more important.

If we look at T_{-2} and take only second order contributions of (7) we get

$$f_{-2}(E_i, 0) = d(0) \frac{1}{8} \alpha^2 p^2 \left\{ \theta(E_i - E_T) - 2\theta(E_i - E_T - \omega) + \theta(E_i - E_T - 2\omega) \right\}$$

This is a positive plateau between E_T and $E_T + \omega$ and a negative plateau of the same absolute value between $E_T + \omega$ and $E_T + 2\omega$ and it is 0 otherwise. $T_{-2} = \frac{p_f}{p_i} |f_{-2}(E_i, 0)|^2$ is then just a plateau between E_T and $E_T + 2\omega$. The step in T_{r1} in fig.6 is rounded and therefore a wedge remains at $E_T + \omega$ in T_{-2} in fig.6. This wedge is a left over between two rounded cut offs on both sides. For higher power density in fig.7 again additional threshold effects at other E_i become important in T_{-2} . An analogous reasoning applies to T_{+2} .

For T_0 and R_N both terms in (7) contribute and the relative phase between both terms is either the same as in the radiationless scattering or it is shifted by π . Therefore the shape of the threshold structures is either the same as in the radiationless case or it is just turned upside down as e.g. in R_0 in fig.6 at $E_T \pm \omega$.

For $E_i = 0.607$, $\alpha = 2$, $N = 0$, $\vartheta = \pi$ and excitation of the target the quantity $\vec{\alpha}(\vec{p}_f - \vec{p}_i)$ is just at the first zero of the Bessel function $J_0(\vec{\alpha}(\vec{p}_f - \vec{p}_i))$ and this explains the accidental zero of Q_0 in fig.7.

4. Discussions and conclusions

We have seen that the low frequency approximation given in (3) explains all qualitative features of resonances and thresholds in free-free transitions except the AC Stark shift. The quantitative error of the low frequency approximation - corrected for the AC Stark shift - has always been below a few percent (see fig.9). But the dependence of this error on the various parameters will probably depend on the dimension of the space. Therefore it would not be of general interest to add here a detailed investigation of the numerical error of the low frequency approximation in our 1-dimensional model.

What advice can we give to an experimentalist, who wants to utilize free-free transitions in order to look for resonances and cusps in electron-atom scattering?

The most interesting property of free-free transitions shown in this paper is that only rapidly varying parts of the radiationless scattering causes any free-free signal in forward direction. This fact may be used in an experiment to project out resonances and threshold effects. The price

to pay for this removal of the background is a reduction of the number of electrons which contribute to the signal. As shown in figs. 2-5 the ratio between the resonance height in $T_N, N \neq 0$ and in T_{r1} is 0.1 in the most

favorable cases.

In an experiment it is not possible to measure at an angle of exactly $\vartheta=0$. By proper adjustment of the laser polarization vector $\vec{\epsilon}$ it is possible to fulfil the relation

$$\vec{\epsilon}(\vec{p}_f - \vec{p}_i) = 0 \quad (8)$$

for any choice of \vec{p}_i and \vec{p}_f , just turn $\vec{\epsilon}$ perpendicular to the momentum transfer $\vec{q} = \vec{p}_f - \vec{p}_i$. At the same time we want to see a strong resonance signal and according to (5) $\vec{\epsilon} \cdot \vec{p}_f$ and $\vec{\epsilon} \cdot \vec{p}_i$ should be big enough to give a big value for the Bessel functions. Therefore, $\vec{\epsilon}$ should be as parallel to \vec{p}_f and \vec{p}_i as possible. All these conditions can be met best if \vec{p}_f and \vec{p}_i are as parallel to each other as the construction of the electron spectrometer allows and if $\vec{\epsilon}$ is in the direction exactly in between \vec{p}_f and \vec{p}_i .

As indicated by the figs. 2-5 resonance signals are biggest and clearest in T_{+2} or T_{-2} at $E_i = E_R - \omega$ or $E_i = E_R + \omega$ respectively if the laser power density is so big that $\vec{\alpha} \cdot \vec{p}_f$ and $\vec{\alpha} \cdot \vec{p}_i$ are in between 1.5 and 2.2 i.e. if $J_1(\vec{\alpha} \cdot \vec{p})$ is near its first maximum. In this case the resonance signal comes from the term $J_{\pm 1}(\vec{\alpha} \cdot \vec{p}_f) f_{r1}(E_i \pm \omega, \vartheta) J_{\pm 1}(\vec{\alpha} \cdot \vec{p}_i)$ in (5). This means: The electron comes in shifted by one photons energy away from the resonance energy. Then it absorbs/emits one photon and can go into the resonance state. The resonance decays and the outgoing electron absorbs/emits another photon on its way out. For this choice of the parameters the resonance signal in $T_{\pm 2}$ is about 10% of the resonance signal in the radiationless scattering, which is the best one

can hope for. In addition, for these values of the parameters the other resonance structures in $T_{\pm 2}$ (i.e. the ones at $E_R, E_R \pm 2\omega, E_R \pm 3\omega$, etc.) are quite small and this decreases the sources of confusion if several elastic resonances occur close together.

For the investigation of thresholds choose a moderate power density of the laser so that only first order contributions give a strong signal to the free-free amplitudes and look at T_{+1} or T_{-1} for structures of the length ω . Two sharp drops in T_{+1} at $E_a - \omega$ and E_a and a smooth behavior in between indicate a threshold at E_a . A similar structure in T_{-1} between E_a and $E_a + \omega$ indicates the same threshold at E_a .

As indicated in figs. 6-8 the absolute signal in $T_N, N \neq 0$ is extremely weak but the relative threshold effect is 1 and can therefore be seen clearly. This is in sharp contrast to elastic scattering where the relative threshold effects are generally small. Usually these effects are observed in electron impact excitation, where their relative effect is bigger than in the elastic channel. Our idea is unusual in so far that it filters out threshold effects in a process which is elastic with respect to the electron-target interaction. The big disadvantage of our method is the extremely small absolute size of the signal and there is the possibility that in a real experiment machine noise will bury the weak threshold signal and make it impossible to utilize our idea in the laboratory.

In any case for resonances or thresholds the photon energy should be chosen larger than the energy interval over which the radiationless scattering varies rapidly in order to avoid confusing overlaps of the structures in free-free transitions.

Can "accidental" zeros like the one in Q_0 shown in fig.7 (i.e. those values of parameters for which $\vec{\alpha}(\vec{p}_f - \vec{p}_i)$ is at a zero of some Bessel function) used for anything? We don't think so, because their position depends strongly on the exact laser power and in an experiment the laser power varies in time and space and the electrons, collected in the detector, have experienced quite different laser powers during their scattering process. Therefore, such an accidental zero would be completely smeared out in any real experiment.

There is also the interesting possibility that a free-free experiment might be used to probe the laser field strength. In ref.11 it has been shown how the results of a measurement of $|f_N(E_i, \vartheta)|^2$ as function of N can be used to calculate the average power density of the laser field in which the experiment has been performed. It is probably possible to generalize the results of ref.11 and to work backwards to even more detailed information about the laser field.

Appendix

In this section we explain our model in detail and show how we calculate the amplitudes for all processes.

We work in a 1-dimensional space and choose x as space coordinate. We describe the electron-target interaction by a 2-channel square well potential of the form

$$V(x) = \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix} \cdot \Theta(R - |x|) \quad (A1)$$

$V_{12}=V_{21} \in \mathbb{R}$ so that V is a self adjoint operator.

Θ is the unit step function. The matrix of excitation energies is

$$B = \begin{pmatrix} 0 & 0 \\ 0 & E_{12} \end{pmatrix} \quad (A2)$$

We cut the x -axis into the three intervals

$$I_1 = (+R, \infty), \quad I_2 = (-R, +R), \quad I_3 = (-\infty, -R)$$

The target is in its ground state initially and the electron comes in with momentum k_{in} . Then the matrix of the electron momentum in intervals I_1 and I_3 is

$$K = \begin{pmatrix} k_o & 0 \\ 0 & k_o \end{pmatrix} = \begin{pmatrix} k_{in} & 0 \\ 0 & \sqrt{k_{in}^2 - 2mE_{12}} \end{pmatrix} \quad (A3)$$

In I_2 we set $M = B + V$ and construct the orthogonal matrix U which diagonalizes M according to

$$U^+ M U = \Sigma \quad \text{with} \quad \Sigma = \begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix} \quad (A4)$$

$[k_{in}^2 \mathbb{1} - 2m \Sigma]^{\frac{1}{2}}$ is the diagonalized momentum matrix in I_2 .

We assume a single mode laser field and use the dipole approximation.

The total Hamiltonian \mathcal{H} for the motion of the electron under the simultaneous influence of the target and the laser field is

$$\mathcal{H} = \left\{ \frac{p^2}{2m} + \hbar \omega a^+ a - \frac{ep}{mc} \beta (a^+ + a) \right\} \mathbb{1} + \mathcal{B} + V(x) \quad (A5)$$

β is an abbreviation for $\beta = (2\pi c^2 / \omega L^3)^{\frac{1}{2}}$ where L^3 is the quantization volume of the electromagnetic field. p is the electron momentum operator, a and a^+ are the annihilation and creation operators for a laser photon. We write $|N\rangle$ for an eigenstate of $a^+ a$ with eigenvalue $N \in \mathbb{N}$.

First let us look at eigenfunctions of \mathcal{H} in the intervals I_1 and I_3 . There \mathcal{H} is diagonal with respect to the target states. We neglect photon depletion effects in the sense that we set $\sqrt{N+n} = \sqrt{N}$ in the coupling strength between various photon number states, where N is the initial number of photons in the laser beam and $N+n$ is the number of photons in intermediate or final states. Using the recursion formula of the Bessel functions

$$2n J_n(y) = y \{ J_{n-1}(y) + J_{n+1}(y) \} \quad (A6)$$

we see that functions of the form

$$\varphi(k_0, x, N) = \exp(ik_0 x) \sum_n J_n(\alpha k_0) |N+n\rangle \quad (A7)$$

are eigenfunctions of the operator

$$\frac{p^2}{2m} + \hbar \omega a^+ a - \frac{ep}{mc} \beta (a^+ + a) \quad (A8)$$

with eigenvalue

$$N\omega + k_0^2 / 2m \quad (A9)$$

α is an abbreviation for $\alpha = e\sqrt{N}2\beta / mc \hbar \omega$.

The quantity $2\beta\sqrt{N}$ is the amplitude of the corresponding classical vector potential A of the laser field. Note that k_0 is independent of n in (A7) because recoil effects of the electron are neglected in dipole approximation. In order to start from the most general eigenfunctions of H we must consider that the functions φ in (A7) are degenerate in two ways:

- 1.: φ remains an eigenfunction of operator (A8) to the same energy (A9) if we reverse k_0 i.e. if we replace k_0 by $-k_0$.
- 2.: We get an eigenfunction to the same energy if we replace N by $N+L$ and simultaneously replace k_0 by k_L where $k_L^2 / 2m + L\omega = k_0^2 / 2m$

Therefore the most general eigenfunction of H with eigenvalue E in the interval I_1 is the 2 component column vector

$$\vec{\Phi}_1(E, x) = \sum_L \begin{pmatrix} r_{1,L} \varphi(k_L, x, L+N) + w_{1,L} \varphi(-k_L, x, L+N) \\ r_{2,L} \varphi(h_L, x, L+N) + w_{2,L} \varphi(-h_L, x, L+N) \end{pmatrix} \quad (A10)$$

where all k_L and h_L are given by

$$E = k_L^2 / 2m + (N+L)\omega = h_L^2 / 2m + (N+L)\omega + E_{12} \quad (A11)$$

$r_{i,L}$ and $w_{i,L}$ are arbitrary complex constants to be fixed later by boundary conditions.

In a completely analogous way we find for the most general eigenfunction of H with eigenvalue E in interval I_3

$$\Phi_3(E, x) = \sum_L \begin{pmatrix} j_{1,L} \varphi(k_L, x, L+N) + t_{1,L} \varphi(-k_L, x, L+N) \\ j_{2,L} \varphi(h_L, x, L+N) + t_{2,L} \varphi(-h_L, x, L+N) \end{pmatrix} \quad (A12)$$

$j_{i,L}$ and $t_{i,L}$ are again constants to be fixed later by boundary conditions.

In the interval I_2 H is not diagonal with respect to target states but $U^\dagger H U = \tilde{H}$ and therefore we first construct eigenfunctions to \tilde{H} . In the same way as before we find for the most general eigenfunction of \tilde{H} with eigenvalue E

$$\tilde{\Phi}_2(E, x) = \sum_L \begin{pmatrix} a_{1,L} \varphi(\lambda_L, x, L+N) + b_{1,L} \varphi(-\lambda_L, x, L+N) \\ a_{2,L} \varphi(\mu_L, x, L+N) + b_{2,L} \varphi(-\mu_L, x, L+N) \end{pmatrix} \quad (A13)$$

$$\text{where } \lambda_L^2 / 2m(N+L)\omega + \sigma_1 = E = \mu_L^2 / 2m(N+L)\omega + \sigma_2 \quad (A14)$$

with σ_1 and σ_2 given in (A4).

$a_{i,L}$ and $b_{i,L}$ are again constants to be fixed later by boundary conditions.

$$\text{Because of } H U \tilde{\Phi}_2 = U \tilde{H} \tilde{\Phi}_2 = E U \tilde{\Phi}_2$$

we see that $\Phi_2 = U \tilde{\Phi}_2$ is an eigenfunction of H with eigenvalue E in interval I_2 .

At $x=+\infty$ we choose the boundary condition that there is only one incoming wave with the target in state 1 and the laser and electron in state $\varphi(-k_{in}, x, N)$ i.e.

$$w_{i,L} = \delta_{i,1} \delta_{L,0} \quad (A15)$$

At $x=-\infty$ we choose the boundary condition that there is no incoming wave at all from the left i.e.

$$j_{i,L} = 0 \text{ for all } i \text{ and all } L \quad (A16)$$

At $x=+R$ and $x=-R$ we require that the wavefunction Φ is

continuous and has a continuous first derivative. This gives 4 equations for 2-component column functions or 8 equations for linear combinations of photon number states. These equations must be fulfilled for the coefficients of each photon state separately and therefore each photon state gives us 8 equations which connect the constants $a_{i,L}, b_{i,L}, t_{i,L}, r_{i,L}$ ($i=1,2$). Some of these equations are inhomogeneous.

Al together, we get an infinite inhomogeneous system of linear equations to determine the free constants. In our model calculations we could only handle a finite number of equations with a finite number of unknowns and therefore we had to cut off the system of equations. Out of the coefficient matrix of the system of linear equations we have cut out the $(2l+1) \cdot 8 \times (2l+1) \cdot 8$ matrix centered at the 8×8 block which comes from the $L=0$ terms in $(A10, A12, A13)$ and the $n=0$ terms in $(A7)$. Accordingly we have cut out of the inhomogeneity vector a $(2l+1)8$ component piece centered at the block which comes from the $n=0$ terms in $(A7)$. Then we have solved these $(2l+1)8$ coupled linear equations.

We have found rapid convergence of the results with increasing l values as soon as $l > |\alpha p|$. For all calculations shown in figs. 2-9 it has been sufficient to choose a l value between 5 and 10. The rapid convergence can be understood from the fact that Bessel functions decrease rapidly as soon as the absolute value of the order becomes larger than

the absolute value of the argument. If we take a larger value of l , then we include coefficients which contain Bessel functions of higher orders.

As a last step we calculate the quantities

$$R_L = \frac{k_L}{k_{in}} |r_{1,L}|^2, \quad Q_L = \frac{h_L}{k_{in}} |r_{2,L}|^2$$

$$T_L = \frac{k_L}{k_{in}} |t_{1,L}|^2, \quad S_L = \frac{h_L}{k_{in}} |t_{2,L}|^2$$

These are the quantities plotted in figs. 2-9 as function of the incoming electron energy E_i .

All these calculations can also be performed for the case that the target is in state 2 initially. The only change is to replace K of (A3) by

$$K = \begin{pmatrix} k_0 & 0 \\ 0 & h_0 \end{pmatrix} = \begin{pmatrix} \sqrt{k_{in}^2 + 2mE_{12}} & 0 \\ 0 & k_{in} \end{pmatrix}$$

and to replace (A15) by

$$w_{i,L} = \delta_{i,2} \delta_{L,0}$$

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Figure captions

Fig.1:Plot of the diagonal elements of the model potential for electron-target interaction used in all numerical calculations.The offdiagonal elements $V_{12}=V_{21}$ (not plotted in fig.1) are of the same shape as V_{11} but of different depth.Bound states of the 1-channel potential $V_{22}+E_{12}$ become Feshbach type resonances of the full coupled 2-channel potential.Their width Γ is determined by the magnitude of V_{12} .For small V_{12} we find $\Gamma \propto (V_{12})^2$.See the two resonances in the upper lines of fig.2 and fig.4. A threshold effect occurs at the rim of the upper well i.e. at $E=E_{12}$.

Fig.2:Plots of resonance structures in radiationless scattering and in free-free transitions.For more explanations see main text.

Fig.3:Plots of resonance structures in free-free transitions.For more explanations see main text.

Fig.4:Plots of resonance structures in radiationless scattering and in free-free transitions.For more explanations see main text.

Fig.5:Plots of resonance structures in free-free transitions.For more explanations see main text.

Fig.6:Plots of threshold structures in radiationless scattering and in free-free transitions.For more explanations see main text.

Fig.7:Plots of threshold structures in free-free transitions.For more explanations see main text.

Fig.8:Plots of threshold structures in free-free transitions.For more explanations see main text.

Fig.9:Some examples for the AC Stark shift of resonances in free-free transitions.The solid lines are the results of numerical calculations.The broken lines are the results of eq.(3).For more explanations see main text.

Fig. 1

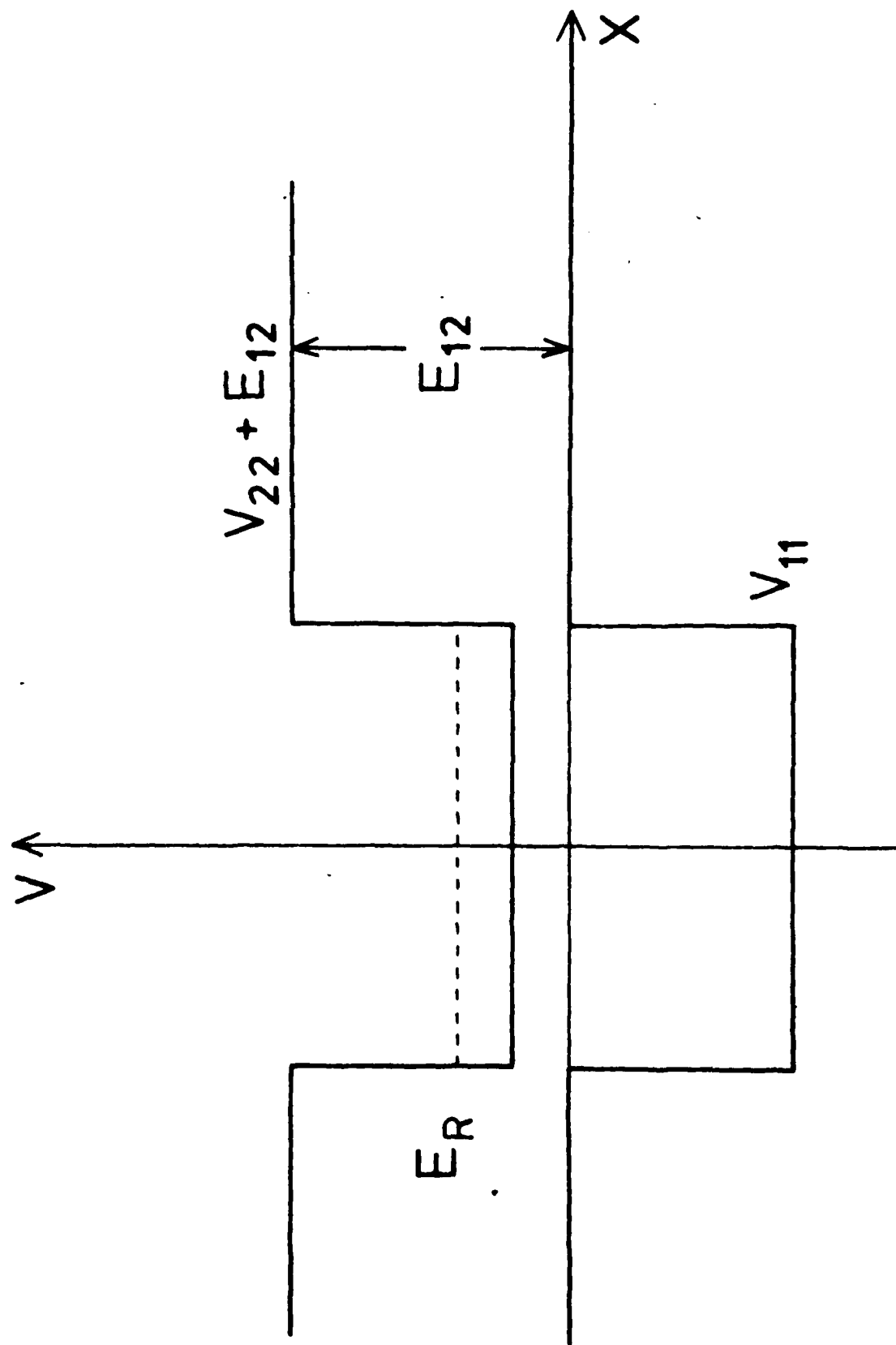


Fig. 2

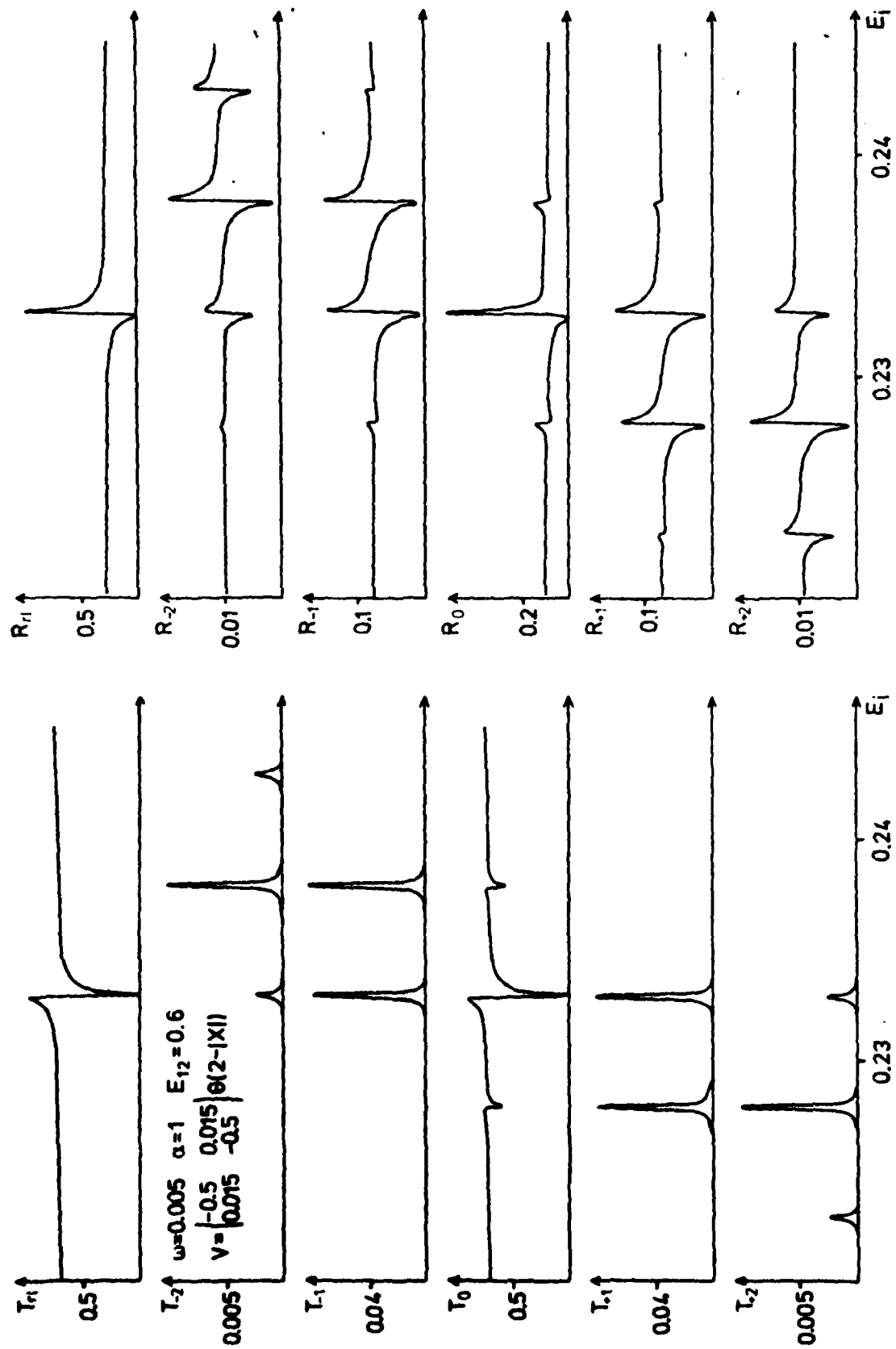


Fig. 3

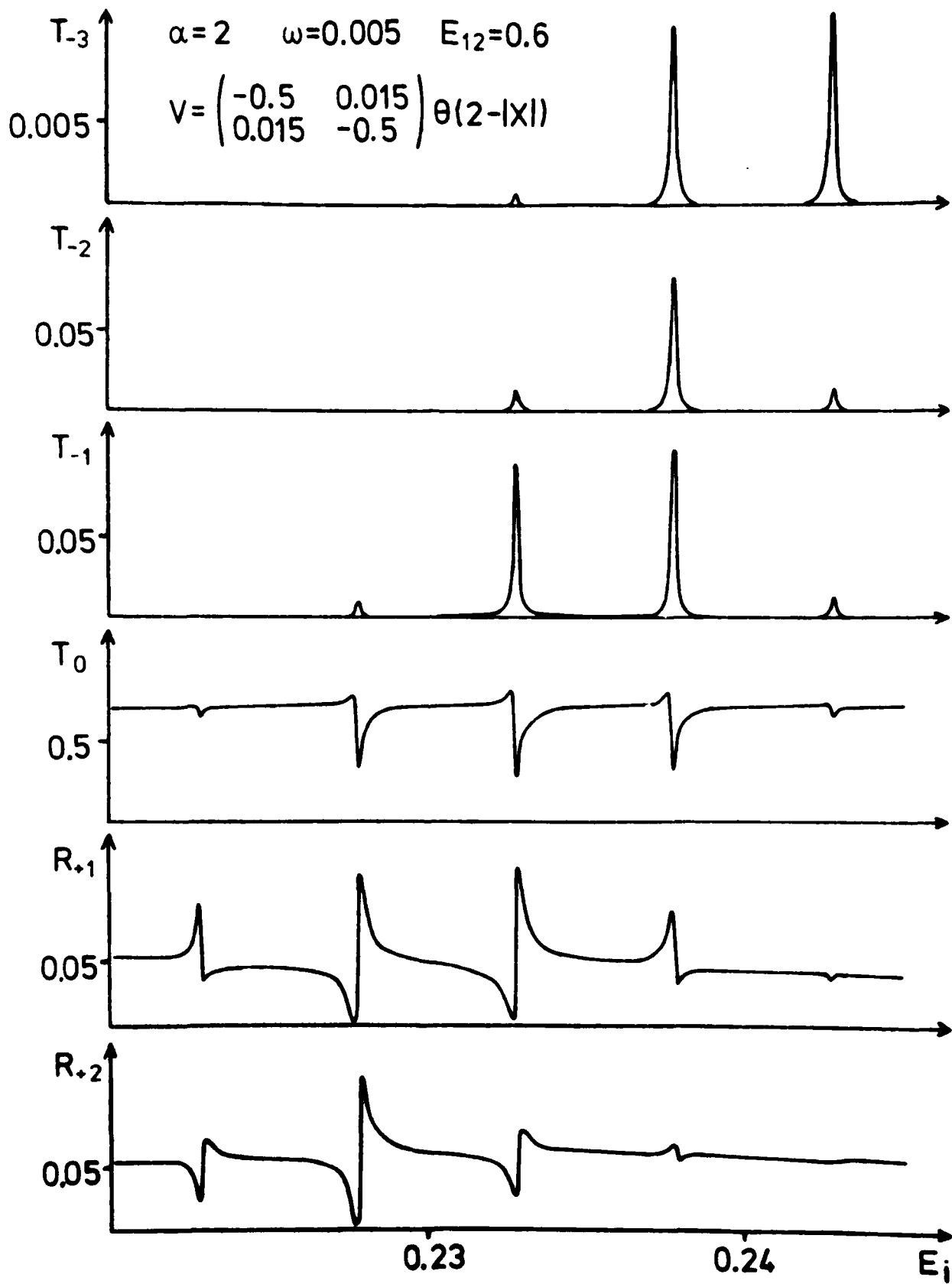


Fig. 4

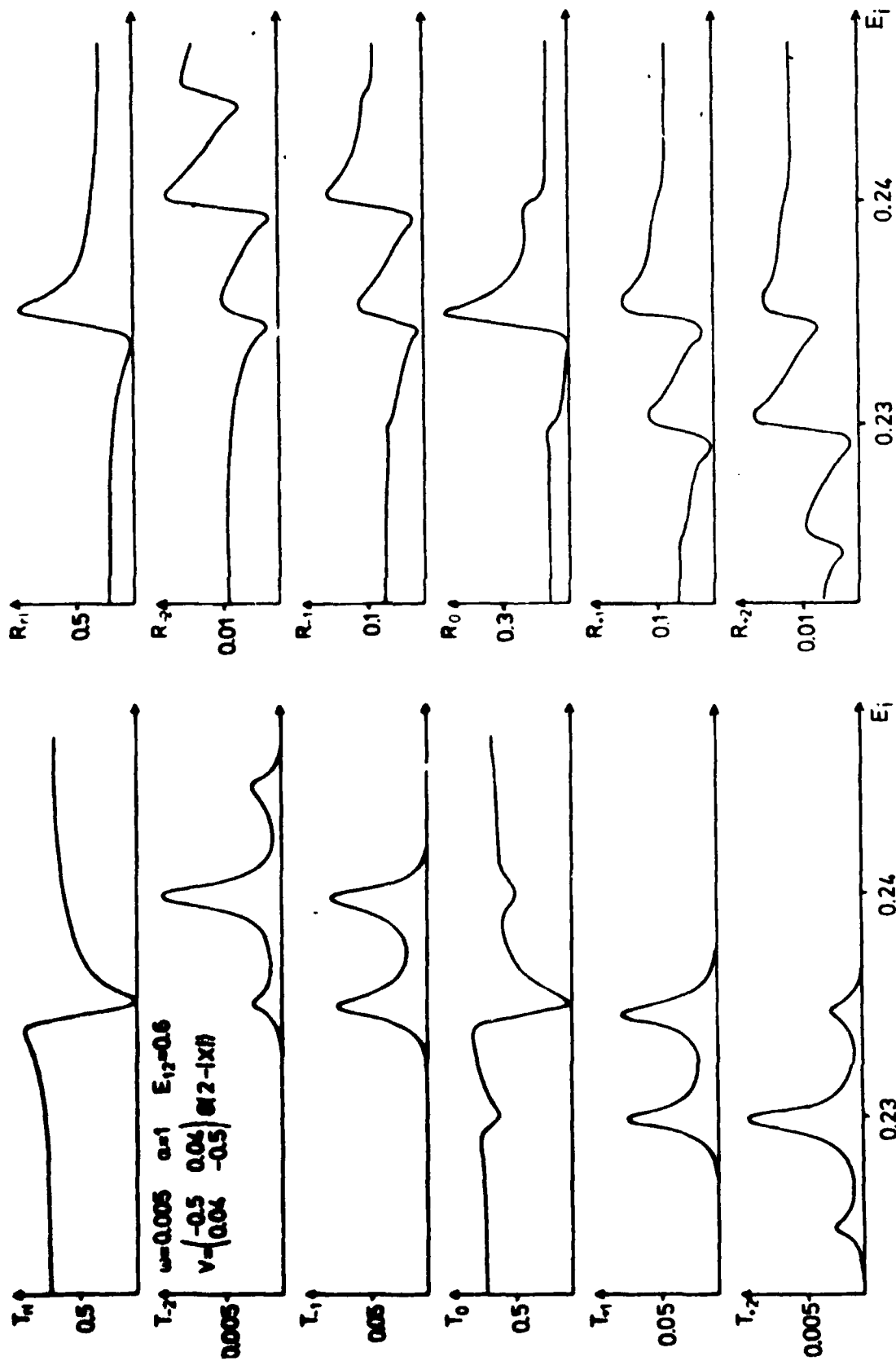


Fig. 5

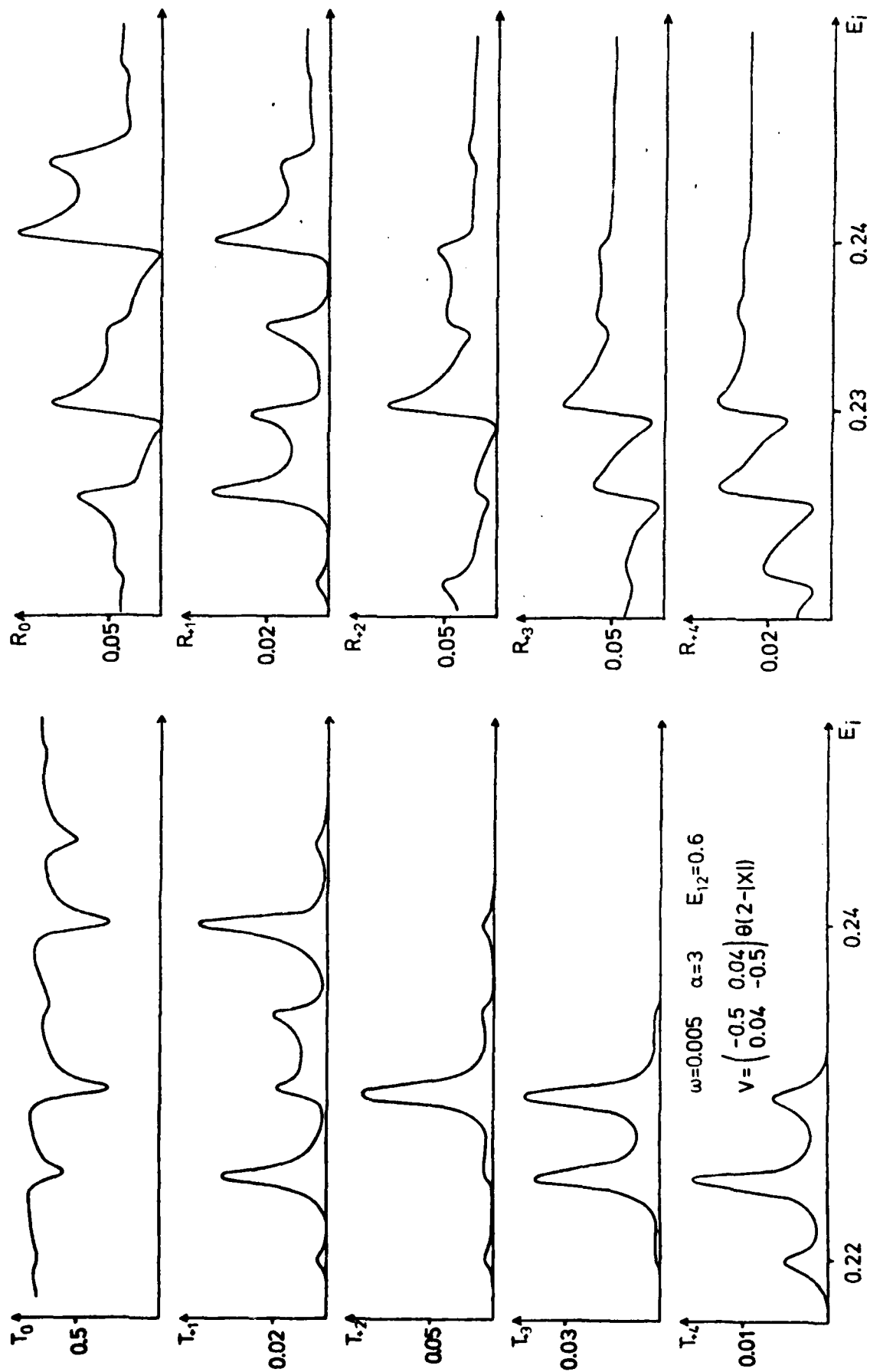


Fig. 6

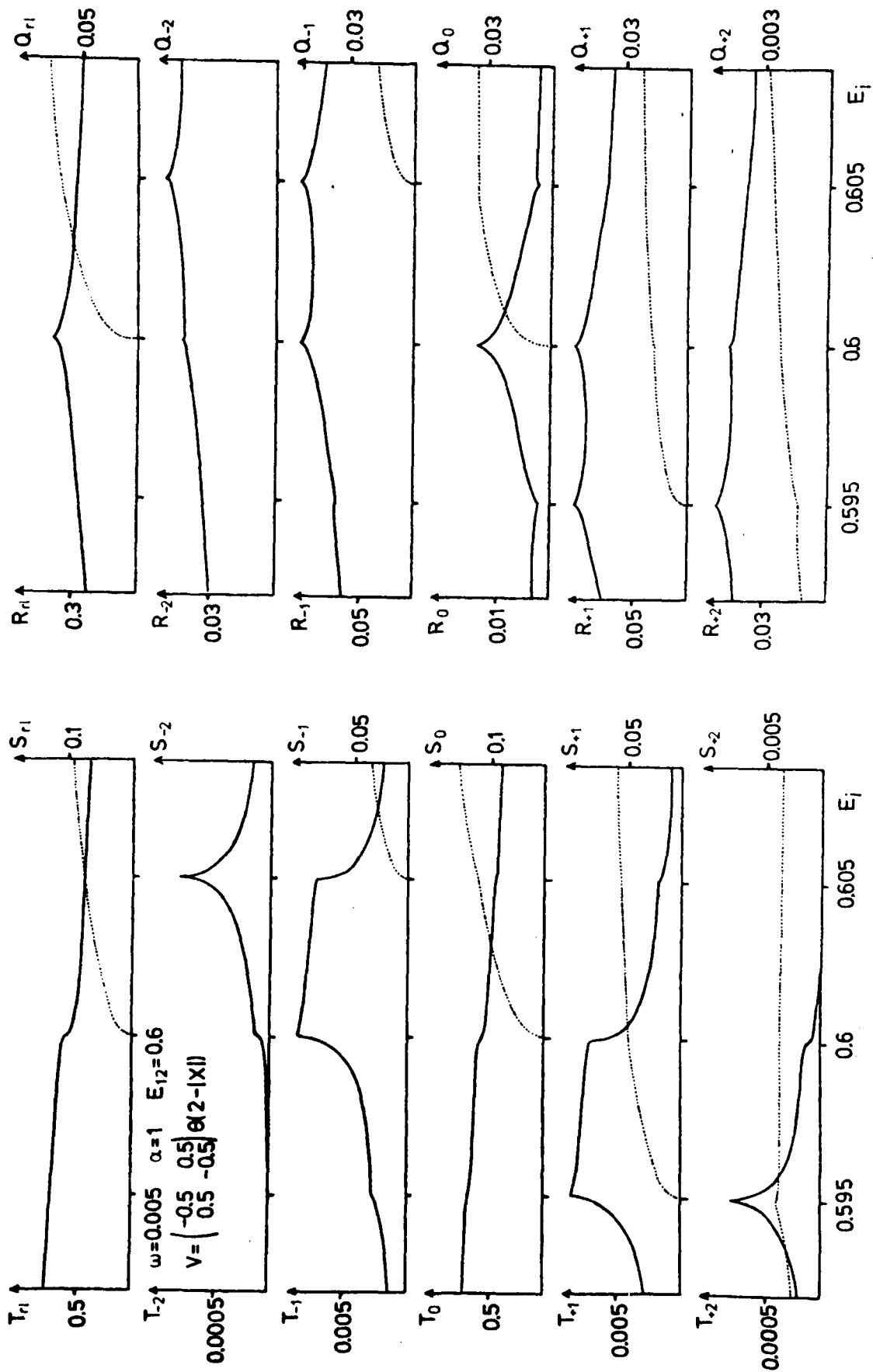


Fig. 7

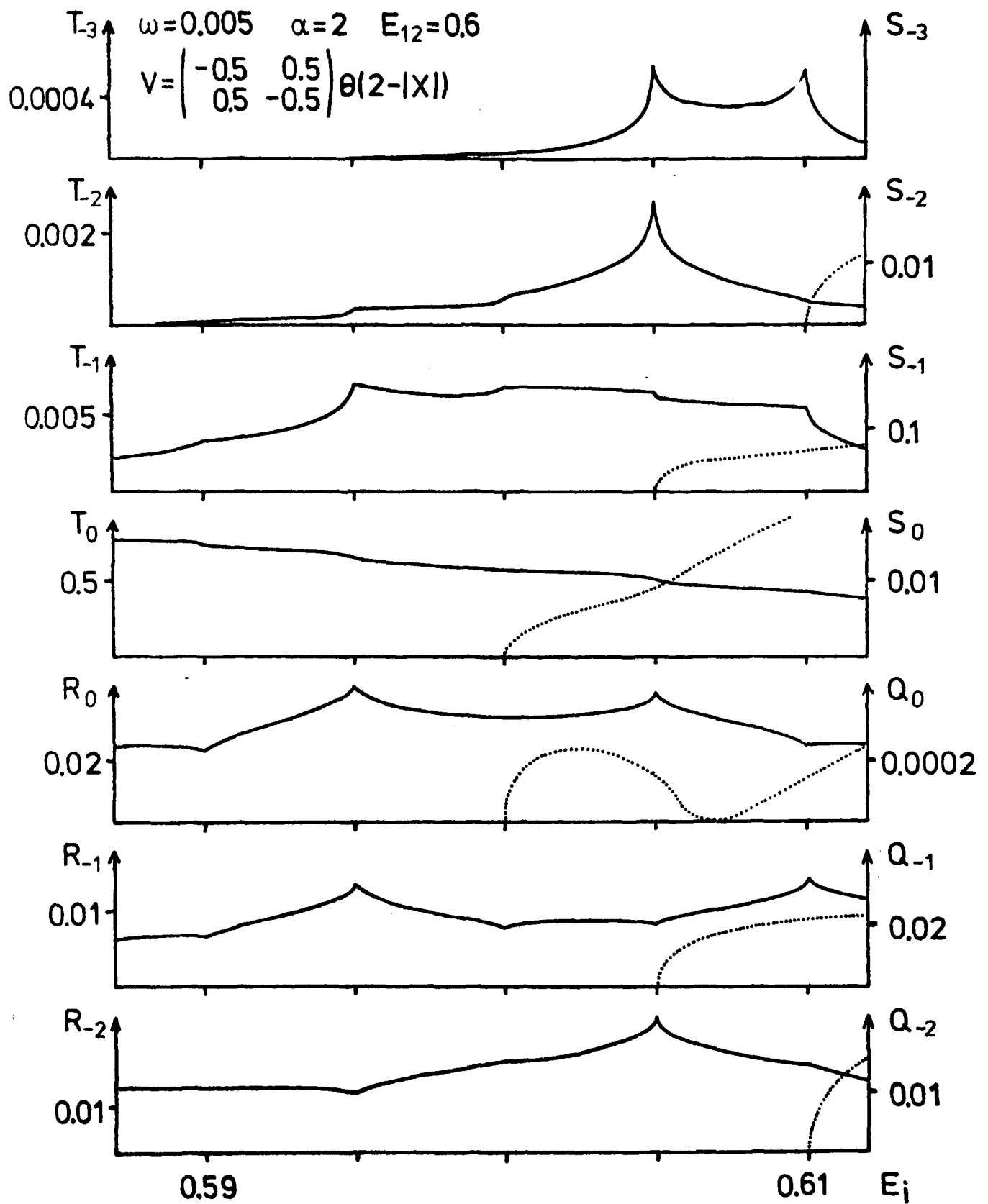


Fig. 8

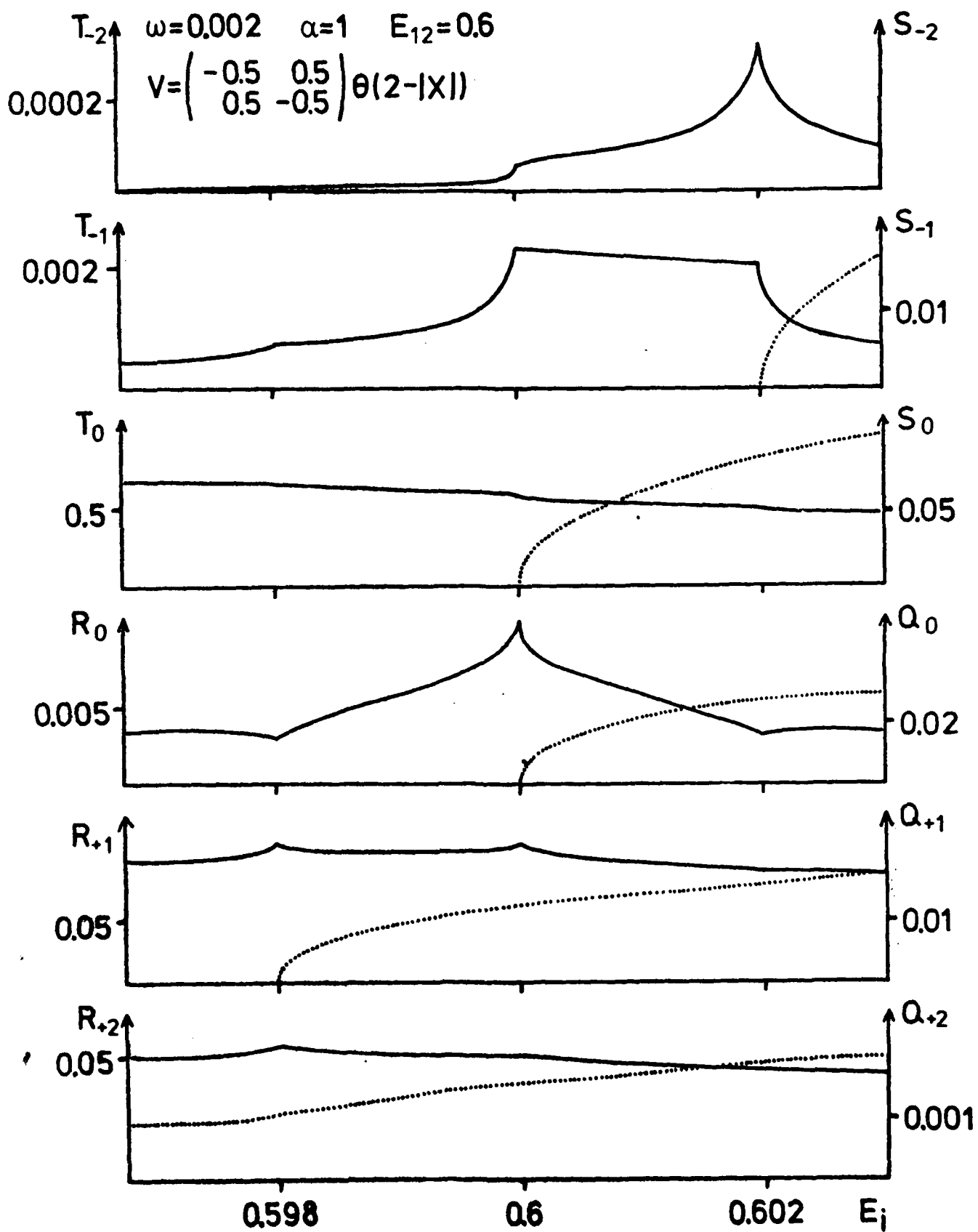


Fig. 9

